THE MECHANISM OF HYDROQUINONE ASSISTED PHOTODEGRADATION OF PVC

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AUGUST 2002

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ABSTRACT

THE MECHANISM OF HYDROQUINONE ASSISTED

PHOTODEGRADATION OF PVC

SİNAN BALCI

M. S. in Chemistry

Supervisor: Prof. Dr. Şefik Süzer

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Pure poly(vinyl chloride) (PVC) degrades upon exposure of UV radiation (λ <300 nm) by the loss of HCl and formation of long conjugated structures known as polyenes. The mechanism of this process is fully understood and known as the zip mechanism, firstly involving the elimination of chlorine radical from the PVC backbone and then the formation of HCl. Addition of chromophores (light absorbing units) into the matrix of the PVC increases the wavelength absorption of the matrix. One of these compounds is Hydroquinone (HQ), which sensitizes the photodehydrochlorination of PVC at 312 nm.

The purpose of this thesis is to shed light into the mechanism of HQ assisted photodehydrochlorination of PVC at 312 nm. Accordingly, the effect of (i) the minimum concentration of HQ, (ii) the temperature of the medium on the rate of PVC photodegradation, (iii) the viscosity of the PVC, (iv) the flux of the irradiation, and (v) the hydroquinone-benzoquinone composition on the rate of PVC photodegradation are investigated. Various sensitizers and quenchers are also used to compare the HQ's sensitisation ability and to investigate the effect of the triplet-state of HQ in the mechanism of the HQ sensitized PVC photodegradation. UV-Visible, IR, and XPS spectroscopic techniques are used to determine the effect of the mentioned parameters.

In the light of all the findings, a mechanism of the HQ assisted (sensitized) photodegradation is proposed to involve mostly formation of a triplet state of HQ followed by effective transfer of this energy to the PVC matrix for dehydrochlorination.

Keywords: Poly(vinyl chloride), hydroquinone, methyl violet, polyaniline, sensitization, quenching, photodegradation, UV-Visible, IR and XPS.

ÖZET

HQ YARDIMIYLA FOTOBOZUNAN PVC POLİMERİNİN MEKANİSMASI

SİNAN BALCI
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Saf poli(vinil klorür) (PVC) mor ötesi ışınlarına maruz bırakıldığı zaman (λ<300 nm) HCl gazı çıkartarak bozunur ve kalan malzeme içerisinde uzun konjüge yapılar olan polienler oluşur. Bu olayın mekanizması bilinmektedir ve zip (fermuar) mekanizması olarak adlandırılır. Bu mekanizmada önce Cl radikali polimerden kopar ve daha sonra HCl oluşur. Kromoforların (ışık soğurucu moleküller) PVC matriksine eklenmesiyle matriksin soğurduğu ışığın dalga boyu artar. Bu özelliği sağlayan maddelerden en önemlilerinden birisi de hidrokinon (HQ) olup PVC polimerinin 312 nm de bozunmasını hızlandırır.

Bu tezin amacı HQ yardımıyla 312 nm de bozunan PVC'nin bozunma mekanizmasının açığa çıkarılmasıdır. Bu nedenle; (i) yeterli en az HQ konsantrasyonu, (ii) sıcaklığın PVC foto bozunmasına etkisi, (iii) PVC viskositesinin önemi, (iv) ışınlama akısının etkisi, (v) matriks içindeki hydrokinon-benzokinon oranının etkileri araştırıldı. Bir çok hızlandırıcı ve yavaşlatıcı maddeler, HQ'nun hızlandırıcı kabiliyetini karşılaştırmak ve triplet durumunun mekanizmadaki rolünü belirlemek için kullanılmıştır. Mor ötesi-Görünür, Kızıl ötesi, ve XPS spektroskobik yöntemleri yukarıdaki faktörlerin etkilerini bulmak için kullanılmıştır.

Bütün bu bulunanların ışığında, önerilen bir bozunma mekanizması ile HQ'nun triplet durumdan geçtiği ve ışıkla alınan enerjinin PVC'ye aktarılarak PVC'nin bozunumunu hızlandırdığı öne sürülmüştür.

Anahtar Kelimeler: Poli(vinil klorür), hidrokinon, metil violet, polianilin, hızlandırma, yavaşlatma, foto bozunma, Mor ötesi-Görünür, IR ve XPS.

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1. INTRODUCTION

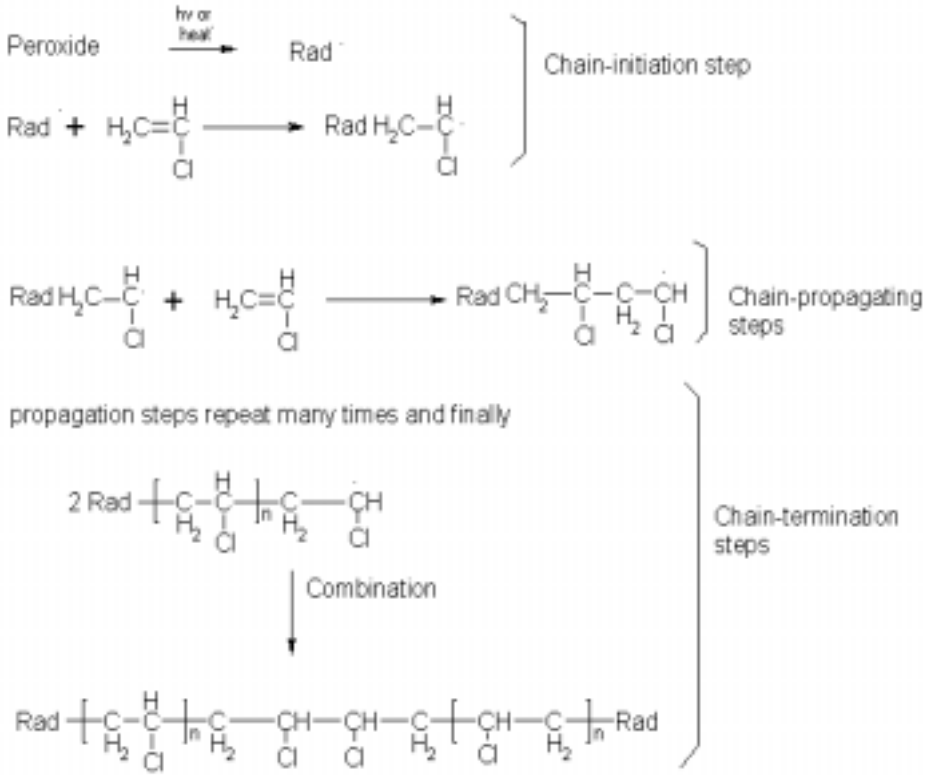
1. 1. Poly(vinyl chloride)

Poly(vinyl chloride) (PVC) is the second most produced and used plastic (polyethylene being the first). Its use is widespread and diverse, ranging from everyday products to highly specialized applications. The building and construction sector (piping, guttering, window profiles, wall plates) makes the broadest use of PVC. Other important applications are flooring and wall coverings, electrical cables, consumption goods, packaging, cars (bumpers, interiors), furniture coverings, tubes and medical applications (blood bags).

It's generally accepted that 1912 was the year PVC was discovered; in fact, it was in this year that Fritz Klatte reported a production process for it. However, PVC was actually in use more than a century earlier. In 1795, four Dutchmen named Dieman, Trotswyck, Bondt, and Laurverenburgh prepared a substance that was named after them "the oil of the Dutch chemists" (dichloroethane). The nature of this substance became the subject of a chemistry debate. Several chemists began working on this issue and in 1835 Henri Regnault produced a gas that burned with a yellow flame with a green mantel (presumably vinyl chloride). In 1860, Hoffman observed that vinyl-bromide, a colorless liquid, changed into a white porcelain-like mass. This process was a mystery to him, and he referred to it as a "metamorphosis ". In 1872, Baumann, elaborating on these results, became the first to make PVC, a white milky precipitate made by putting tubes filled with vinyl chloride in direct sunlight [1].

1. 1. 1. Preparation

PVC is produced from vinyl chloride monomers by free radical vinyl polymerisation. In this polymerisation, reaction initiators, free radicals, are generated from the peroxides by using light or heat. The mechanism of the free radical polymerisation of PVC is shown in



Scheme 1: Free radical polymerization of PVC [2, 3].

Scheme 1. Polymerisation involves addition of free radicals to the double bond of the monomer: addition, first, of the free radical generated from the initiators, and then of the growing chain of polymer molecule. In each step the consumption of a free radical is accompanied by the formation of a new, bigger free radical. Eventually, the reaction chain is terminated by steps that consume but do not form free radicals: combination of two big free radicals.

During the polymerisation chain transfer, the termination of one polymerisation chain with the simultaneous initiation of another can decrease the degree of polymerisation. In order to control the degree of polymerisation sometimes inhibitors, an added compound reacting with the growing free radical to generate a new free radical that is not reactive enough to add to monomer, are added to the reaction vessel after desirable properties are obtained [3, 4].

In modern industry PVC is produced by suspension polymerisation. Polymerisation of vinyl monomers in solution is advantageous from the standpoint of heat removal and control. Bulk polymerisation of vinyl monomers is more difficult compared to solution polymerisation in that the reactions are highly exothermic and, with the usual thermally decomposed initiators, proceed at a rate, which is strongly dependent on temperature.

Because heat control during the polymerisation of vinyl monomers is an important step for the production of high quality PVC, very large-scale tank reactors are used. Water and vinyl chloride monomers are loaded together with the initiator and other recipe ”ingredients”. The reaction mass is heated up to temperature T_e, that is kept constant by balancing the generated and evacuated heat. The heating-cooling jacket works as an overflow loop, the flow rate of the external thermal agent F_s being controlled to achieve the reaction heat balance. An external condenser can remove the heat of polymerisation by monomer condensation. The reactor pressure is constant during the polymerisation, but shows a sharp decline after a critical conversion X_c. At this point the polymerisation rate reaches its maximum and here the heat removal may be critical. The final conversion is slightly above 90 %. The times to reach the critical conversion and final polymerisation are characteristic for operation. A good operation should maximise the reaction rate while respecting product specification and a thermal regime [4, 5]

1. 2. Polymer Degradation

In synthetic macromolecules polymer degradation refers to the changes in physical properties caused by chemical reactions involving bond scission in the backbone of the macromolecule. In linear polymers, these chemical reactions lead to a reduction in molecular weight:

Scheme 2: Main-chain scission of the polymer backbone [6].

Scheme 2 shows the main-chain scission of the polymer backbone. When considering biopolymers, the definition of polymer degradation is extended to include changes of physical properties, caused not only by chemical but also physical reactions, involving the breakdown of the higher ordered structures. In both cases the term polymer degradation involves deterioration in the functionality of the polymeric materials.

Intermolecular crosslinking, i.e. the formation of new chemical bonds between individual macromolecules, may be considered the opposite of degradation as it leads to an increase in molecular size and, at higher conversions, to certain kinds of superstructures with characteristic physical properties.

It seems appropriate to point out that the expression scissions, rupture, breakage and lesion are used synonymously to indicate bond fracture in the splitting of chemical bonds in the backbone or main-chain of linear polymers.

Polymer degradation is mainly caused by chemical bond scission reactions in macromolecules. It is useful to subdivide this broad field according to its various modes of initiation. These comprise [6]:

Chemical degradation
Thermal degradation
Mechanical degradation
Photodegradation
Degradation by high-energy radiation

Chemical degradation refers exclusively to processes, which are induced under the influence of chemicals (e.g. acids, bases, solvents, reactive gases, etc.) brought into contact with polymers. In many such cases, a significant conversion is observed, however, only at elevated temperatures because the activation energy for these processes is high.

Thermal degradation refers to the case where the polymer, at elevated temperatures, starts to undergo chemical changes without the simultaneous involvement of another compound. Often it is rather difficult to distinguish between thermal and thermo-chemical degradation because polymeric materials are only rarely pure. Impurities or additives present in the material might react with the polymeric matrix, if the temperature is high enough.

Mechanically initiated degradation generally refers to macroscopic effects brought about under the influence of shear forces. Apart from the important role polymer fracture plays in determining the applications of plastics, it should also be pointed out that stress induced processes in polymeric materials are frequently accompanied by bond ruptures in the polymer main-chains. This fact can be utilized for the mechanochemical initiation of polymerisation reactions with the aim of synthesizing block-and graft- copolymers.

Light-induced polymer degradation, or photodegradation, concerns the physical and chemical changes caused by irradiation of polymers with ultraviolet or visible light. In order to be effective, light must be absorbed by the substrate. Thus, the existence of chromospheric (light absorbing unit) groups in the macromolecules (or in the additives) is a prerequisite for the initiation of photochemical reactions. Generally, photochemically important chromophores absorb in the ultraviolet region. The importance of photodegradation of polymers derives, therefore, from the fact that various polymeric materials can absorb the ultraviolet portion of the sunlight spectrum. The resulting chemical processes may lead to severe property deteriorations.

High-energy radiation such as electromagnetic radiation (X-rays, γ-rays) or particle radiation (α-rays, fast electrons, neutrons, nuclear fission products), is not specific with respect to absorption. The existence of chromospheric groups is not prerequisite as in the case of photodegradation since all parts of the molecule are capable of interacting with the radiation. The extent and character of chemical and physical changes depend on the chemical composition of the irradiated and the nature of the radiation [6].

1. 2. 1. Photodegradation

Most commercial polymers undergo chemical reactions upon exposure to the ultraviolet light, since they have chromophoric groups capable of absorbing UV light. This fact is important because the spectrum of the sunlight passing the earth atmosphere contains a portion of UV light. Therefore, photoreactions are usually induced when organic polymers are subjected to outdoor exposures. In general, photoreactions in commercial

polymers are harmful: they cause embrittlement and color changes. Since the large-scale production of organic polymers, the producers have invested on the prevention of photodegradation. In this respect, photolytic reactions of special importance are UV light initiated oxidative chain reactions.

Apart from deterioration effects, the field of photodegradation comprises beneficial aspects also. A typical example is the utilization of readily degradable polymers as positively acting resists for the production of solid-state electronic microstructures.

It is appropriate to emphasize here two important aspects [6, 7]:

(i) the specific interaction of light with organic compounds and

(ii) the randomness of photochemical reactions in polymer.

Light absorption in a molecule consists of a specific interaction of a certain chromophoric group with a photon of given energy. The remainder of the molecule remains unaffected during the absorption activity. If a polymer chain is supposed to be ruptured at a certain position on irradiation, this goal can be achieved by synthetically introducing an appropriate chromophore at that place in the polymer backbone.

The second aspect, referred to above, derives from the fact that light is absorbed statistically by the chromophores in a system. All that we know is the probability for the absorption of a certain photon by a certain chromophore. There is an equal probability of absorption of a photon by the chromophore in the polymeric matrix. Therefore, chemical reactions occurring subsequent to light absorption can be initiated at any place at the backbone of the polymer.

1. 2. 2. Light Absorption and Quantum Yield

The absorption of light is prerequisite for the occurrence of photochemical reactions. Saturated compounds possessing bonds such as C-C, C-H, O-H, C-Cl absorb light at

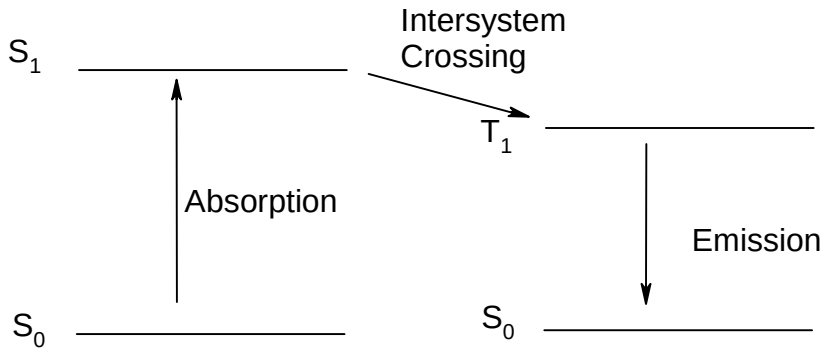


Figure 1:Energy-state diagram indicating important photophysical processes

λ<200nm. Carbonyl groups and conjugated bonds such as C=C bonds absorb above λ>200nm and have absorption maxima between 200nm and 300nm [6]. The chance of an absorbed photon to induce a chemical change in the molecule depends principally on the photophysical processes following the absorption activity. Figure 1 shows the energy state diagram. According to this diagram, the absorption of photon can proceed either as $S_0 + h\nu \Longrightarrow S_1$ or $S_0 + h\nu \Longrightarrow T_1$. The extinction coefficients differ appreciably: $\varepsilon(S_0 \Longrightarrow S_1) >> \varepsilon (S_0 \Longrightarrow T_1)$ [6, 7]. Therefore, $S_0 \Longrightarrow T_1$ processes are negligible with respect to photochemical changes. Because of their very long life times, chemical reactions originate from S_1 or T_1 states. T_1 states are very long-lived owing to the fact that transitions of the type $T_1 \Longrightarrow S_0$ are forbidden. Internal conversions are very rapid processes. Radiative and radiationless deactivation processes of S_1 states occur very rapidly. Generally, fluorescence occurs much faster than phosphorescence. It is possible to determine the absorbed dose quite accurately, i.e. the number of photons absorbed per unit mass or unit volume by a sample during irradiation. The unit is Einstein that is the one mole of photons. Scheme 3 describes the important photophysical processes. The

Photon	$^1M + h\nu \rightarrow {}^1M^*$ (1^{st} excited singlet state)
Absorption	$^1M + h\nu \rightarrow {}^1M^{**}$ (higher excited singlet state)
	$^1M + h\nu \rightarrow {}^2M^{+}. + e^-$ (Photoionization)
Radiationless	$^1M^* \rightarrow {}^1M$ + energy (internal conversion)
Transitions	$^1M^* \rightarrow {}^3M^*$ + energy (intersystem crossing)

	$^1M^{**} \rightarrow {}^1M^* +$ energy (internal conversion)
	$^3M^{**} \rightarrow {}^3M^* +$ energy (internal conversion)
Luminescence	$^1M^* \rightarrow {}^1M + h\nu$ (fluorescence)
(Radiative Transitions)	$^3M \rightarrow {}^1M + h\nu$ (phosporescence)

Scheme 3: Important photophysical processes [7, 8].

conversion is expressed as the quantum yield, i.e. the number of atoms or molecules converted per photon absorbed by the irradiated material. In the photodegradation of polymers, the quantum yield for main-chain scission, $\phi(S)$ [6], for example, denotes the number of main-chain scissions per photon absorbed by the polymer.

1. 2. 3. Energy Transfer and Migration

Figure 2 shows the possible pathways of a photon absorbed by a homopolymer, i.e. by a polymer composed of identical repeat units. Since each repeating unit contains the same chromophore, excitation energy can travel down the chain. It is important to distinguish energy migration, i.e. transfer of electronic excitation energy between like molecules, from energy transfer between like molecules. Energy migration down the polymer chain is a polymer-specific process [7]. Principally, there are two types of action with respect to energy transfer and polymer degradation [7, 8]:

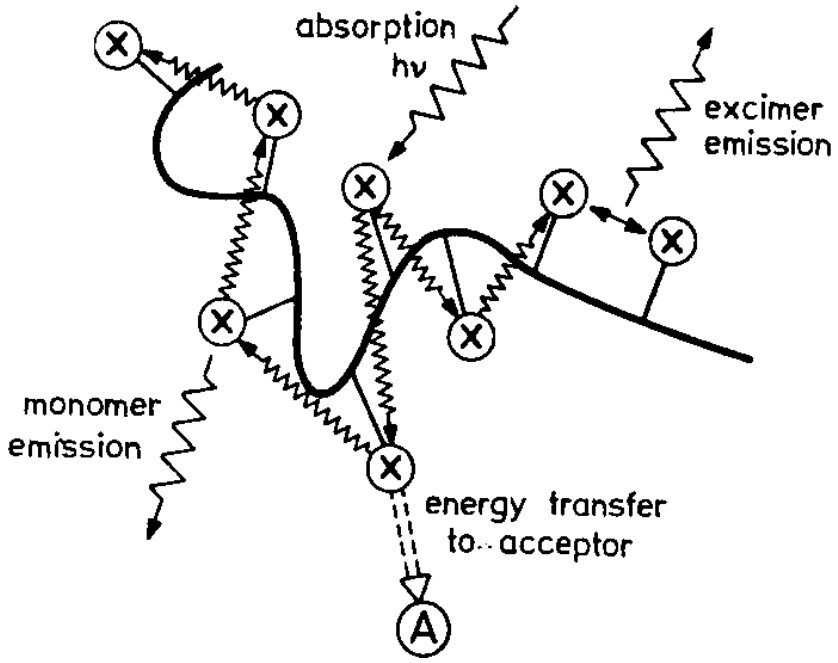


Figure 2: Schematic illustration of intramolecular energy transfer and migration in polymers [6].

(I) Sensitization:

$S + h\nu \Longrightarrow S^*$ (1.2)

$S^* + P \Longrightarrow S + P^*$ (1.3)

Exited polymer molecules P* are generated via reaction (1.3) and can undergo chemical reactions.

(II) Protection:

$P + h\nu \Longrightarrow P^*$ (1.4)

$P^* + Q \Longrightarrow P + Q^*$ (1.5)

Exited polymer molecules P* are quenched by an additive Q according to reaction (1.5), which implies the inhibition of chemical reactions of P* [7, 8]. Introducing quenchers can block sensitization of the photochemical processes.

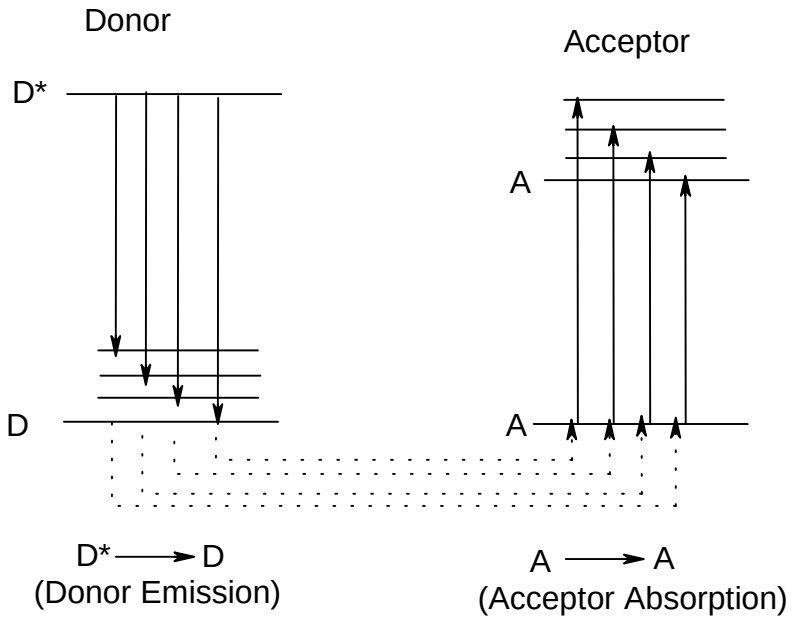


Figure 3: Schematic illustration of corresponding transitions in energy transfer.

Energy transfer processes, described generally by reaction (1.6) are generally

$$D^* + A \Longrightarrow D + A^* \qquad (1.6)$$

(D=Donor, A=Acceptor, astheric=electronically exited state)

determined by reaction energies. Energy transfer occurs isoenergetically, i.e. the transition energies D* ==>D and A ==> A* must match perfectly. Figure 3 depicts the related transitions in exothermic energy transfer. Corresponding energy levels must exist in donor and acceptor molecules. Energetically allowed transitions are given by the spectral distribution of the donor emission, f_D, and the respective distribution of acceptor absorption, f_A. The spectral overlap integral provides (1.7) a measure of the overlap of donor emission and acceptor absorption spectra. If J=0, energy transfer is impossible

$$J=\int f_D f_A dv \qquad (1.7)$$

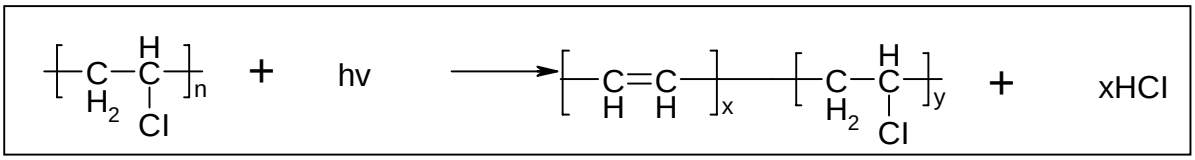
For J= 0, the magnitude of the rate constant of reaction (1.7) depends on the specific mechanism [2, 7, 8].

1. 2. 4. Photodegradation of PVC

Photodegradation (photooxidative degradation) and photodehydrochlorination of poly(vinyl chloride) and its copolymers and blends have been discussed in a number of reviews, and books, and were the subject of many experimental publications [9-15].

The potential of a polymer for light-induced degradation is determined by its ability to absorb photons of suitable energy and availability of photochemical pathways to utilize the absorbed energy for chemical reactions. The Grotthus-Draper law states that only the radiation absorbed by a system is effective in producing chemical changes. Most polymers can absorb ultraviolet (UV) radiation of $\lambda < 300$ nm [10], while those with chromophores such as carbonyl groups and unsaturated centers can absorb even longer wavelengths of (UV) radiation. The photon energies associated with the near ultraviolet (UV) and visible radiation are in the same range as the bond dissociation energies of common covalent bonds in organic molecules including polymers. PVC contains only C-C, C-H, and C-Cl, bonds and is therefore not expected to absorb light of wavelength longer than 300 nm [11]. The fact that free radicals are formed after irradiation of longer wavelength indicates that some kinds of chromophores must be present in the polymer matrix. The light and heat instability of PVC must be caused by structural abnormalities that are present to varying extents in different types of commercially available polymer samples such as unsaturated end groups, branch points, random unsaturation, and oxidized structures such as hydroperoxide groups and carbonyl groups [9-11].

It is generally accepted that photodegradation and phototermal degradation occurs with discoloration of the polymer due to the polyene formation (Scheme 4)[12, 13].



Scheme 4: Polyene formation during degradation of PVC.

These yellow-brown-colored polyene structures consist of 2-14 conjugated bonds, and measuring UV-Visible absorption spectra can monitor their formation.

The role of oxygen in the photodecomposition of PVC is complex. It has been found that oxygen [14]:

(I) Decreases the energy of activation.

(II) Accelerates the rate of dehydrochlorination reaction.

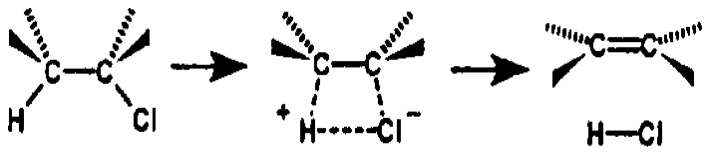
(III) Causes bleaching by attacking the polyene structures and shortening the length of conjugation.

(IV) Promotes chain scission and crosslinking.

As a result of photooxidation of PVC, hydroperoxide (OOH) and carbonyl (C=O) groups are formed [13].

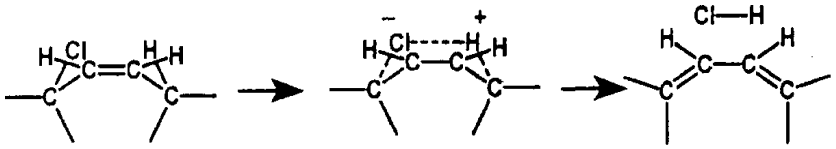
Gel permeation chromatography (GPC) analysis shows a broadening of the molecular weight distribution of the photooxidised PVC towards both lower and the higher molecular weights, thus indicating that crosslinking competes with the chain scission process [12-14].

Molecular orbital calculations at the Modified Neglect of Diatomic Overlap (MNDO) level with AM1 or PM3 parameterization give enthalpies for chloroalkanes and chloroalkenes dehydrochlorination. Table 1 depicts the dehydrochlorination enthalpies of chloroalkanes and corresponding alkenes, Table 2 depicts the dehydrochlorination enthalpies of chloroalkenes and corresponding alkenes in the gas phase. Dehydrochlorination of chloroalkanes is a molecular 1,2-elimination through a four-center transition state (Scheme 5).



Scheme 5: 1,2-elimination of HCl from the alkyl chloride.

The transition state, for chloroalkanes, requires very strong polarization of the carbon-chlorine bond. In the case of allyl chlorides, they eliminate hydrogen chloride in a 1,4-process through a six-center transition state generated from a cis-configuration of the double bond (Scheme 6). The corresponding transition state requires much lower activation enthalpy and less polarization of the molecule than the 1,2-elimination of the



Scheme 6: 1,4-elimination of HCl from the allyl chloride.

chloroalkanes. On the other hand, if allylic chlorine atoms have a trans configuration, elimination of chlorine atoms from the molecule is not easy like in the case of cis-configuration since trans-chlorine atoms are as stable as the normal chain residues. This explains why in PVC dehydrochlorination, systems of 1-25 conjugated double bonds are formed. Formation of double bond sequences larger than 25 double bonds have a negligible probability [15].

Table1: Activation enthalpies for dehydrochlorination of chloroalkanes in gas phase [15].

Chloroalkane	Alkene	$\Delta H_{experimental}$ (kJ/mol)	$\Delta H_{Calculated}$ (kJ/mol)
1) Chloroethane	Ethene	242.7	245.6
2) 1-Chloropropane	Propene	227.6	244.4
3) 2-Chloropropane	Propene	202.1	215.5
4) 1-Chlorobutane	1-Butene	234.7	239.7
5a) 2-Chlorobutane	Trans-2-butene	213.8	222.6
5b) 2-Chlorobutane	Cis-2-butene	218.0	226.4

Table 2: Activation enthalpies for dehydrochlorination of chloroalkenes in gas phase [15].

Chloroalkene	Alkene	$\Delta H_{experimental}$ (kJ/mol)	$\Delta H_{Calculated}$ (kJ/mol)
1) 4-Chloro-1-butene	1,3-Butadiene	227.6	232.6
2) 3-Chloro-1-butene	1,3-Butadiene	200.4	184.0
3) 3-Chloro-1-pentene	Cis-1,3-pentadiene	210.0	196.2
4) 3-Chloro-1-pentene	Trans-1,3-pentadiene	141.4	186.6
5) Cis-4-chloro-2-pentene	Cis-1,3-pentadiene	141.4	139.3
6) Trans-4-chloro-2-pentene	Trans-1,3-pentadiene	194.6	186.6

1. 3. Photosensitization

The term photosensitizer describes a chemical compound or a chemical system, which sensitizes (photosensitizes) photoreaction by an energy transfer mechanism. Electronic energy transfer is the one-step transfer of electronic excitation from an excited donor molecule (D*) to an acceptor molecule (A) in separate molecules (intermolecular energy transfer) or indifferent parts of the same molecule (intramolecular energy transfer):

$D + h\nu \rightarrow D^*$

$D^* + A \rightarrow D + A^*$

Electronic transfer process may occur by the following mechanisms.

(I) radiative energy transfer

(II) non-radiative energy transfer

Various factors affect the extent and rate of energy transfer between an excited donor (D*) and the acceptor (A):

(I) distance between D* and A

(II) relative orientation to each other

(III) spectroscopic properties of D and A

(IV) optical properties of the medium

(V) effect of molecular collisions on the motion of the excited donor and an acceptor in the period during which the donor is excited.

In general:

(I) the energy of the excited state (A*) must be lower than that of (D*) in order the energy transfer to be efficient,

(II) the sensitized excitation of A by D* must occur within the time that the molecule D remains in the excited state[16].

1. 4. Aim of the Study

Although previous researchers have mostly tried to stabilize degradation of PVC, our studies concentrated on benefiting from this degradation, such that we can utilize the in-situ photogenerated acid (HCl) to induce optical and/or electrical changes in the polymer matrix [17-20]. The optical changes were followed by acid-base indicators (mainly methyl violet, MV), the electrical changes were achieved by introduction of conducting polymers (polyaniline, PANI) and the photosensitization of PVC was accomplished by introduction of hydroquinone (HQ). Sensitization of photodehydrochlorination of PVC by HQ was demonstrated by Suzer et al. [20]. Although pure PVC does not exhibit any appreciable changes when exposed to either 254 or 312 nm radiations for 120 minutes, a blend containing 10 %(w/w) HQ undergoes extensive dehydrochlorination as well as polyene formation when exposed to 312 nm UV radiation that corresponds to the maximum of HQ absorption. Although the sensitization of HQ at different wavelengths was clearly shown in previous study, detailed mechanism of the process was not explained.

The main goal of this thesis is to explore/understand the detailed mechanism of the HQ assisted PVC dehydrochlorination. The samples were prepared by casting the blends (PVC, PANI, MV and HQ) in tetrahydrofuran (THF). Spectroscopic techniques like FTIR, UV-Vis-NIR and XPS were used to assess the physical and chemical changes.

In order to establish the mechanism of this HQ assisted photodehydrochlorination of PVC, effects of several experimental parameters like; concentration of HQ in the matrix of PVC, benzoquinone-hydroquinone ratio in the PVC matrix, the temperature of the medium, the viscosity of the PVC, the flux of the irradiation need to be investigated in detail.

1. 5. Conducting Polymers

Electronic and optical properties of π-conjugated system have acquired a growing importance in many areas modern chemistry and physics of condensed matter. At the molecular level, they represent the simplest models of molecular wires, which together with their complementary functions such as molecular switches, or logic gates, have contributed to the emergence of the concepts of molecular electronics and logic. The π-system in conjugated polymers gives rise to conductivity, electro- and thermo-chromic effects, electroluminescence, and non-linear optical properties, which are very important in high technological applications. The discovery in 1973 that poly(sulfur nitride) is a metal led the scientists to study the new group of chemical compounds, at the moment known as conducting polymers. Since the initial discovery in 1977, that polycacetylene (CH_x), now commonly known as the prototype conducting polymer, could be p- or n-doped either chemically or electrochemically to the metallic state, the development of the field of the conducting polymers has continued to accelerate at an unexpectedly rapid rate. Also, a variety of other conducting polymers and their derivatives has been discovered since that time. An organic polymer that possesses electrical, electronic, magnetic, and optical properties of metal while retaining mechanical properties, processibility, etc. commonly associated with a conventional polymers, is termed an "intrinsically conducting polymer" more commonly known as a "synthetic metal". Extrinsic conducting polymers can be obtained by doping the intrinsic conducting polymers. By doping, an organic polymer, either an insulator or semiconductor having a small conductivity, typically in the range from 10^{-10} to 10^{-5}S/cm, is converted to a polymer, which is in the metallic conducting regime (~1-10^{4}S/cm). In the undoped state these polymers are wide-band-gap semiconductors and are in the insulating regime. The controlled addition of known, non-stoichiometric quantities of chemical species results in dramatic changes in the electronic, electrical, magnetic, optical, and structural properties of the polymer. There are several kinds of doping methods [21]:

-Chemical and electrochemical p-doping

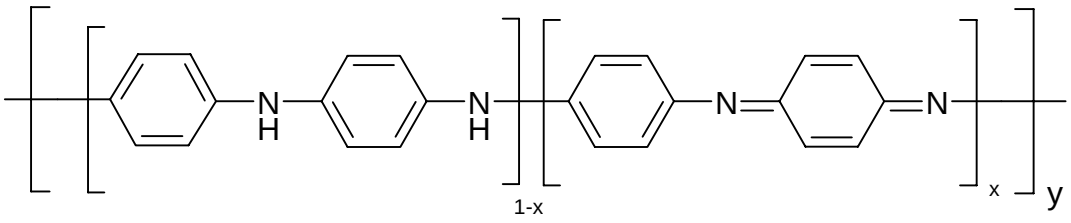
-Chemical and electrochemical n-doping

-Photo-doping

-Charge-injection doping

-Non-redox doping

Of the conducting polymers polyaniline (PANI) is among the most studied ones. The general formula for the PANI is shown in Scheme 7.



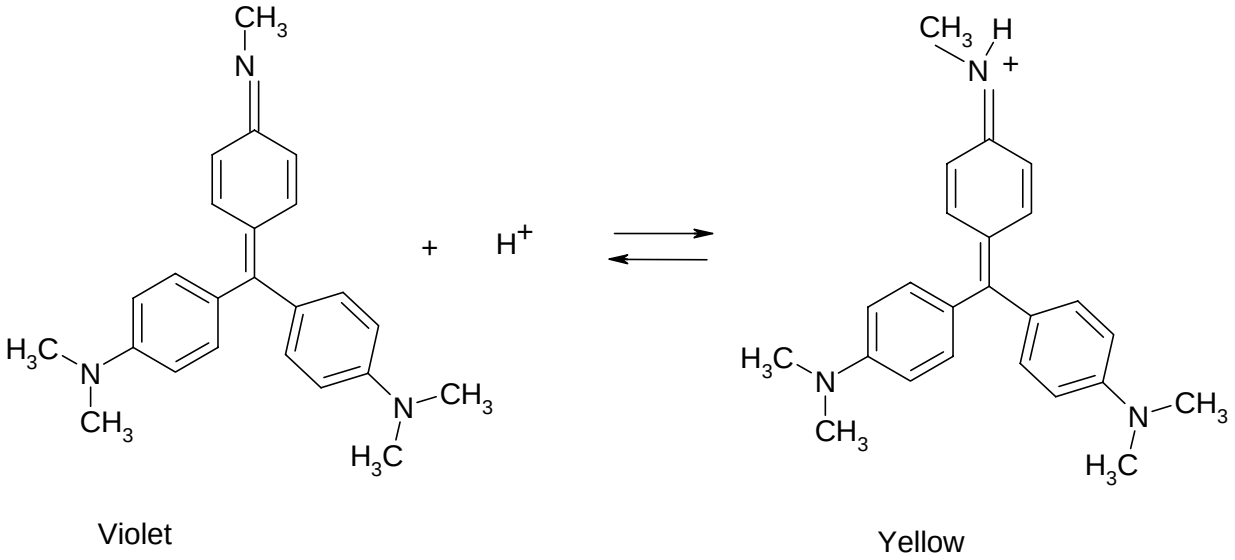
Scheme 7: Oxidized and reduced form of PANI.

This formula consists of alternating reduced and oxidized forms. The terms 'leucoemeraldine', 'emeraldine', and 'pernigraniline' refer to the different oxidized and reduced states of the polymer where (1-x)=0, 0.5, 1, respectively, either in the base form, e.g. emeraldine base, or in the protonated salt form, e.g. the emeraldine hydrochloride. Using the stretching frequency of benzenoid and quinoid forms at 1500 $cm^{-1}$and 1600 cm^{-1} one can follow the degree of oxidation, respectively by IR spectroscopy. It has been found that PANI is most conductive in its green state, emeraldine form, which corresponds to a value of x=0.5. In principle, the imine nitrogen atoms can be protonated in whole or in part to give the corresponding salts, the degree of protonation of the polymeric base depends on its oxidation state and on the pH of the aqueous acid. Complete protonation of the imine nitrogen atoms in emeraldine base by aqueous HCl results in the formation of a delocalized polysemiquinone radical cation. This process is accompanied by an increase in conductivity by several orders of magnitude. Deprotonation of the polymer can be achieved by aqueous ammonium hydroxide to give emeraldine base powder [22-26]. Although conducting polymer films have several useful functions, their poor mechanical properties render them less practical. To improve the properties, the incorporation of a conducting polymer film with a plastic is one of the most promising methods. Unfortunately, however, the electrical conductivity of such a composite film is much lower than that of an original conducting polymer film because the plastic is intrinsically insulating. In the present study, PVC is used as the matrix layer

and PANI as the conducting polymer, showing the manifestation of electrical conductivity of PVC in the composite film. PVC is attractive for this purpose because it can be photo-dehydrochlorinated to a form conjugated polyene structure in the polymeric backbone and because it has reliable mechanical strength and processebility. These facts are favorable for the formation of a composite film with good electrical and mechanical properties [17-20, 26-28].

1. 6. Methyl Violet

Methyl violet is a pH indicator. pH indicators are weak acids or bases. Upon addition of protons they change their intense colors. In this study methyl violet is used because of its UV-Resistance and more importantly its color transition range, which is between pH 0.0



Scheme 8: Acidic and basic forms of methyl violet.

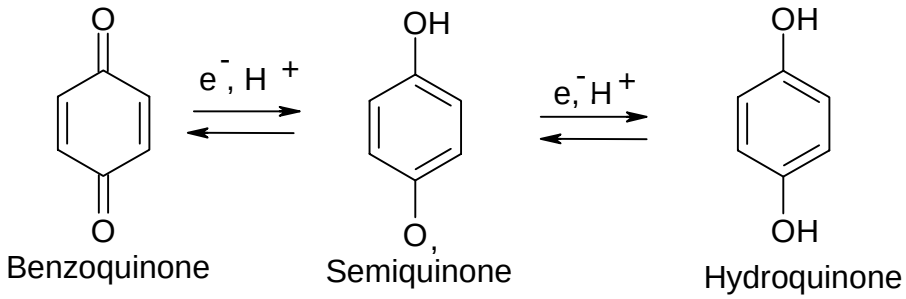
0 and 1.6. Above this range, methyl violet has the violet color and below this range it has yellow color. Scheme 8 shows the structure of the acidic and basic forms of the methyl violet upon addition of the proton [29].

Denman et al. [30] studied the photostability of methyl violet to (UV) and visible radiation in different media. It has been shown that methyl violet undergoes very little

amount of photodecomposition alone. However, in the hydroxyl group-containing medium (hydrogenperoxide), the decomposition increased nearly 100 times.

1. 7. Hydroquinone

It is well known that hydroquinone (HQ) undergoes electrochemical oxidation to benzoquinone (BQ) in aqueous media according to the reaction shown in Scheme 9. This equilibrium reaction has been used for pH measurements because the potential for



Scheme 9: Oxidation of hydroquinone to semiquinone and then benzoquinone.

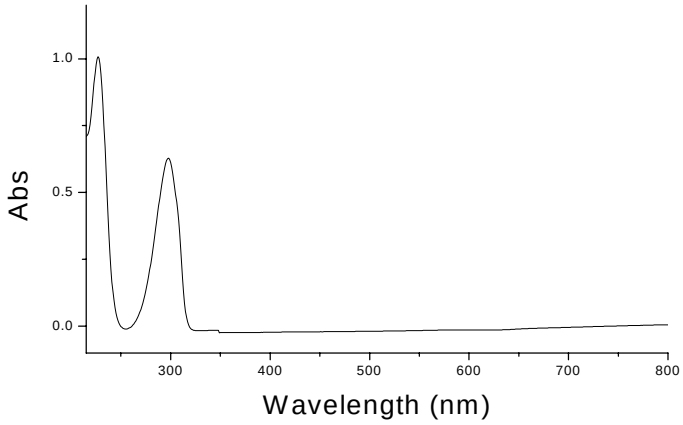


Figure 4: UV-Visible spectrum of the HQ in THF.

the reaction exhibits a pH dependence of 60mV/pH with a proton involved for each electron transfer. The HQ oxidation reaction is also very important in many biological reactions [29]. Shim et al. [31] studied the reduction of BQ to HQ. They found that in buffered solution the reduction is a two-electron process however in unbuffered solution the reduction is one electron process. It is also explained that during the electrochemical reduction of BQ to HQ, first, electron transfer being the main process, second is the protonation of the radical anion. The oxidation of HQ to BQ can be monitored by using electronic spectroscopy. Figure 4 shows the UV-Visible spectrum of the HQ in THF. Oxidized form of the HQ, BQ, having the quinoid structure, has the corresponding UV-Visible spectrum in Figure 5.

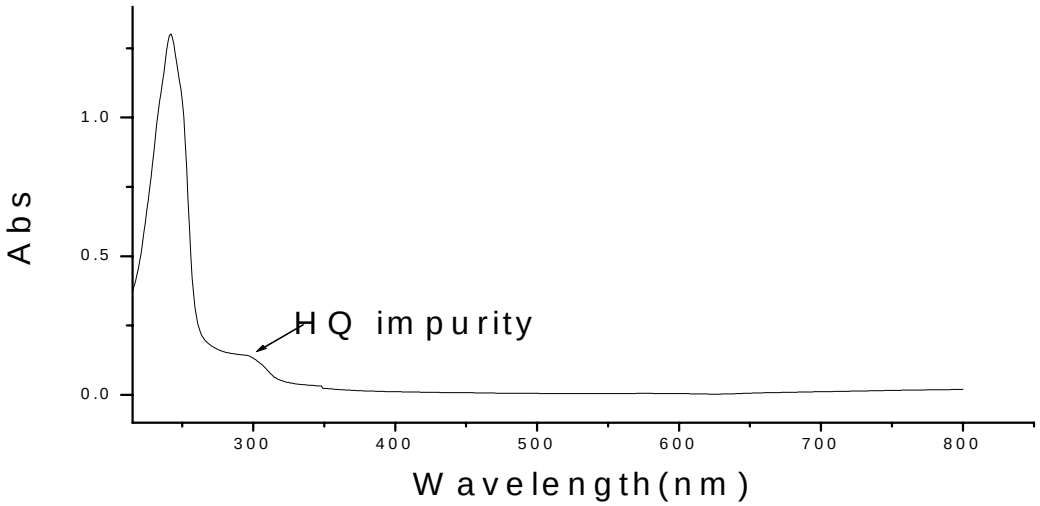


Figure 5: UV-Visible spectrum of the BQ in THF.

1. 8. Electronic Spectroscopy

Electronic spectroscopy deals with the transitions of molecules between different electronic potential wells. An electron is promoted from a low energy orbital to a higher energy orbital. Electronic ground state is the state in which the electrons occupy the lowest energy molecular orbitals. The electrons that contribute to absorption by an organic molecule are those that participate directly in bond formation and nonbonding or unshared outer electrons that are largely localized [32]. Generally, the energy level of the

nonbonding electron lies between those of the bonding and the antibonding π and σ orbitals. Electronic transitions among the energy levels can be brought about by the absorption of radiation. Four types of transitions are possible [33].

$\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$, and $\pi \rightarrow \pi$

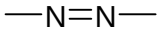
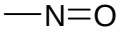
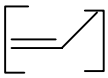
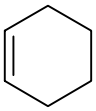
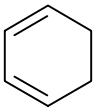
$\sigma \rightarrow \sigma^*$ *transition*: An electron in a bonding σ orbital of a molecule is excited to the corresponding antibonding orbital by the absorption of the radiation. The molecule is then described as being in the σ, σ* excited state. Relative to the other possible transitions, the energy required to induce a σ-σ* transition is large corresponding to frequencies in the vacuum ultraviolet region.

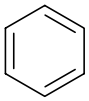
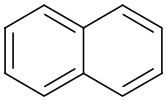
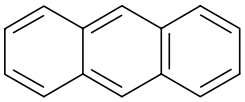
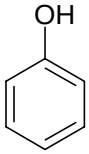
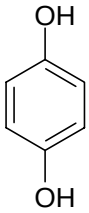
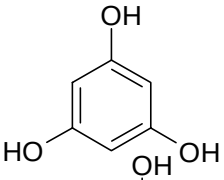
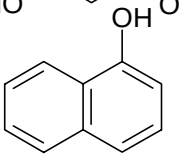
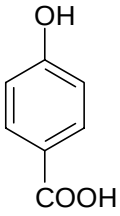
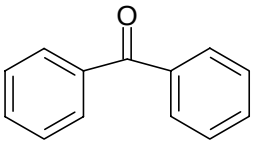
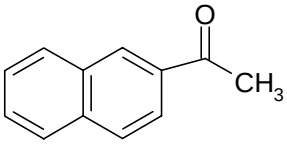
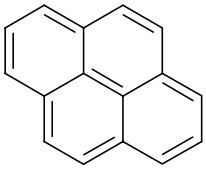
$n \rightarrow \sigma^*$ *transition:* Saturated compounds containing atoms with unsaturated electron pairs (nonbonding electrons) are capable of this type transition. In general, these transitions require less energy than the σ-σ* type and can be brought about by radiation in the region between 150 and 250 nm.

$n \rightarrow \pi^*$ *and* $\pi \rightarrow \pi^*$*transition:* Most applications of absorption spectroscopy to organic compounds are based on the transitions for n or π electrons to the π* excited state, because the energies required for these processes bring the absorption peaks into an experimentally convenient spectral region (200 to 700 nm).

Table 3 lists common organic chromophores and the approximate location of their absorption maxima. These data can serve only as rough guides for the identification of functional groups. The peaks are broad because of vibrational progression. In the molecular-orbital treatment, π electrons are considered to be further delocalised by conjugation. The orbitals involve four (or more) atomic centers. The effect of this delocalization is to lower the π* orbital and give it less antibonding character. Absorption maxima are shifted to longer wavelengths as a consequence [32-35].

Table 3: Absorption characteristics of some common chromophores [35].

Chromophore	Typical compound	Electronic Transition	Maximum Wavelength (nm)
	Ethene	$\pi \longrightarrow \pi^*$	180
	Propanone	$n \longrightarrow \pi^*$	277
		$\pi \longrightarrow \pi^*$	185
	Azomethane	$n \longrightarrow \pi^*$	347
	Nitrosobutane	$n \longrightarrow \pi^*$	665
	-Carothene	$\pi \longrightarrow \pi^*$	497
	1,3-Cyclopentadiene	$\pi \longrightarrow \pi^*$	239
	Cyclohexene	$\pi \longrightarrow \pi^*$	182
	1,3-Cyclohexadiene	$\pi \longrightarrow \pi^*$	256
	1-Octyne	$\pi \longrightarrow \pi^*$	185

	Benzene	$\pi \longrightarrow \pi^*$	200
	Naphthalene	$\pi \longrightarrow \pi^*$	221
	Anthracene	$\pi \longrightarrow \pi^*$	250
	Phenol	$n \longrightarrow \pi^*$	250
	Hydroquinone	$n \longrightarrow \pi^*$	300
	1,3,5-Trihydroxybenzene	$n \longrightarrow \pi^*$	230
	1-Naphtol	$n \longrightarrow \pi^*$	300
	4-Hydroxybenzoicacid	$n \longrightarrow \pi^*$	270
	Benzophenone	$n \longrightarrow \pi^*$	260
	2-Acetonaphtanone	$n \longrightarrow \pi^*$	300
	Pyrene	$\pi \longrightarrow \pi^*$	350

1. 9. Infrared Spectroscopy

Infrared spectroscopy is one of the most powerful tools available to the chemist for identifying pure organic and inorganic compounds because with the exception of a few homonuclear molecules, such as O_2, N_2, and Cl_2, all molecular species absorb infrared radiation. Furthermore, with the exception of chiral molecules in the crystalline state, each molecular species has a unique infrared absorption spectrum. Infrared spectrometers have been commercially available since the 1940s. At that time the instruments relied on prisms to act as dispersive elements, but by the mid 1950s, diffraction gratings had been introduced into dispersive machines. The most important advances in infrared spectroscopy have come about with the introduction of Fourier-transform spectrometers. This technique improved the quality of infrared spectra and minimized the time required to obtain data [32, 33, 36].

1. 10. X-Ray Photoelectron Spectroscopy

Photoelectron spectroscopy (PES), developed about 1960s, studies the kinetic energies of electrons emitted when molecules of a sample are ionized by absorption of high-energy monochromatic radiation. In x-ray photoelectron spectroscopy, x-ray photons (AlKα of 1486.6 eV or MgKα of 1255.6 eV) are used to provide ionization of a gas or solid sample. The high-energy x-ray photons can remove an electron from an inner shell orbital as well as from a valence molecular orbital, so one can obtain binding energies for inner and valence electrons. X-ray photoelectron spectroscopy allows both quantitative and qualitative analysis for elements present in a sample and for this reason, x-ray PES is often called electron spectroscopy for chemical analysis (ESCA). ESCA can give direct chemical states of the element in a sample. In different environments, in different oxidation states and substituents, one can obtain different spectrum of the related element [37].

1. 11. Previous Studies

The majority of investigations of PVC have focused on stabilization [38, 39]. There are also several reports, which have attempted to benefit from PVC dehydrochlorination [10, 17-20, 40-54]. In this section, we will try to sum them up.

PVC, Poly(vinylidene chloride) and further chlorinated products of PVC are dehydrochlorinated (Tsuchida et al. [40]) under appropriate conditions. It is found that elementary analysis of the remaining product fits the formula $(CH)_n$. By using infrared spectra and x-ray diffraction patterns they showed that the structure of the product is similar to that of noncrystalline, trans polyacetylene. The absorption band due to -CH=CH- (trans) is observed for all products. In the products of the further chlorinated polymers; the band due to the triple carbon-carbon bond also appears in the spectra. Using Electron Spin Resonance Spectroscopy (ESR), they also demonstrated the paramagnetic properties of the product.

Physical and electrical properties of polyenes arising from dehydrochlorination of PVC were studied by Soga et al. [41]. PVC samples having various degrees of polymerization were dehydrochlorinated in a mixture of an organic base and a polar solvent to give black powdery polyenes. The polyenes were found to have long sequences of conjugated double bonds. The electrical conductivity did not depend on the molecular weight of the original PVC, and a maximum conductivity of $4x\ 10^{-3} Scm^{-1}$ was obtained after doping with SO_3. They also attempted to utilize them as battery components in the $LiClO_4$ propylene carbonate solution using the polyene as an anode material.

Danno et al. [42] have used 1,8-diazobicyclo[5,4,0] undec-7-ene, the strongest organic base known at that time, to obtain a polyene material having electrical conductivity of 10^{-8}S/cm from PVC films. In this study, the polyene film has a considerable long conjugated sequence but the length of the conjugated chain is very widely distributed. After doping with the iodine, the thin film showed conductivity of 10^{-4} S/cm.

Decker et al. [16] have studied the synthesis of conductive polymers by laser irradiation of chlorinated PVC. The basic idea behind this work is to directly prepare conductive polymers by using as starting material chlorinated PVC that is shown to be a highly photosensitive polymer. Under intense UV irradiation, it is possible to pursue the dehydrochlorination toward its ultimate stage in order to finally end up with a purely carbon polymer. The material obtained is expected to consist mainly of graphite and should therefore be conductive by itself. The first report of such a graphitization of chlorinated PVC is reported which is induced by laser irradiation in order to reach the very high photon density that is required for a complete removal of the H and Cl atoms from the polymer backbone. In a later study, Decker [43] reported on the photochemical modifications of PVC. PVC has been modified by photochemical reactions in order to either produce a conductive polymer or to improve its light-stability. In the first case, the PVC plate was extensively photochlorinated and then degraded by UV exposure in N_2. Total dehydrochlorination was achieved by a short Ar^+ laser irradiation at 488 nm that leads to a pure carbon polymer, which was shown to exhibit an electrical conductivity. In the second case, an epoxy-acylate resin was coated onto a transparent PVC sheet and crosslinked by UV irradiation in the presence of both a photoinitiator and an UV absorber. This superficial treatment was found to greatly improve the photostability of PVC as well as its surface property.

The polyene sequences growth in the dehydrochlorination of PVC was studied by Simon et al. [44]. The syn-elimination of HCl from 4-chloro-1-butene and 1-chlorobutane has been studied by MNDO/3 method. The calculated activation energy for the dehydrochlorination of 4-chloro-1-butene is close to that for 3-chloro-1-butene. This result indicates that, when considering the unimolecular mechanism of PVC dehydrochlorination, polyenes sequence growth both in the direction of the allylic Cl atom and in that of the allylic H atom should be allowed.

Hell et al. [45] have showed that PVC does not crosslink to a useful extent when subjected to irradiation by gamma rays or electrons. The high energy results in several undesired reactions in polymer matrix, which are not desirable for many applications of

PVC. The addition of radiation sensitizers leads to efficient crosslinking by lowering the high energy needed to initiate the crosslinking by using triallyl cyanurate as a sensitizer. By this way they improved the mechanical properties of PVC by lowering the extend of damage that high radiation makes to the PVC matrix.

Stability of the conjugated polyene was studied by Perichaurd et al. [46]. Using NMR and ESR, they have characterized the conjugated system and studied its stability in air. They have shown also that a significant improvement of the stability of the material can be achieved by an appropriate chemical treatment with sulfur. The natural oxidation of the chain by sulfur instead of air oxygen is used to dope the polyene chain through charge transfer and to protect the double bonds against further oxidation.

A new radiochromic dosimeter film is proposed by Sidney et al. [47] by employing acid-base sensitive leuco dyes in chlorine –containing polymer matrix, for gamma, electron beam, and ultraviolet radiation. These dosimeter films undergo a color change from colorless to royal blue, red fuchsia, or black, depending on dye selection, and have been characterized them using a visible spectrophotometer over an absorbed dose range of 1 to 100 kGy. The primary features of the film are improved color stability before and after irradiation, whether stored in the dark or under artificial light, and improved moisture resistance. The effects of absorbed dose, dose rate, and storage conditions on dosimeter performance are discussed. The dosimeter material may be produced as a free film or coated onto a transparent substrate and optionally backed with adhesive. Potential applications for these materials include gamma sterilization indicator films for food and medical products, electron beam dosimeters, and in-line radiation monitors for electron beam and ultraviolet processing.

Ogura et al. [48] have studied a novel preparation of electrically conducting PVC by photo-dehydrochlorination from PVC/PPy composite film. PPy is deposited electrochemically on a platinum plate from a nitric acid solution of pyrrole. The PVC/PPy composite film is finally obtained by casting PVC onto the PPy electrode from a THF solution of PVC. The prepared composite film is irradiated at 90 ^{0}C with a low-

pressure mercury lamp in the stream of hydrogen gas saturated with steam, and the PVC film is dehydrochlorinated, leading to the formation of conjugated polyenes. The electrical conductivity of the PVC film in the irradiated composite film is 2.51×10^{-5} S cm^{-1}. By iodine doping, the conductivity is further enhanced up to 5.04×10^{-3} S cm^{-1}. The tensile strength of the irradiated composite film becomes larger than that of the original PVC film. The doping of radical species to the conjugated polyene brings about these results. The anion, NO_3^-, doped during the electrodeposition of PPy is photodecomposed to generate $NO_2^{\cdot}$ radical. And this species are used to dope the polyenes, resulting in the formation of electrically conductive PVC and mechanically improved composite film.

Kohler et al. [49] have demonstrated the distribution of effective conjugation lengths from absorption spectra of solutions of long linear polyenes. Distributions are found to be dominant by short conjugation lengths. Knowing the absorption spectrum of a linear polyene is dominated by the strongly allowed $1^1 A_g \rightarrow 1^1 B_u$ absorption, the dependence of excitation energy for this transition on the number of double bonds are calculated using (HSS) the Huckel Spectrum Simulator model. They tabulated the absorption of the polyenes for different chain length.

Benavides et al. [50] have studied the stabilization of PVC with pre-heated metal stearates and the effect of carbonyl groups on the polyene formation. PVC films are treated with $NaBH_4$ to eliminate the carbonyl groups. Carbonyl groups attached to polyenes shift the absorbance maxima of the polyenes and also the quantification of the double bond conjugation.

PVC as a photodonor of HCl for protonation of polyaniline is proposed by Sertova et al. [51]. A novel photoinduced protonation of PANI (EB) from PVC as donor of HCl is proposed. The UV-induced protonation of the polymer chain is studied through its optical absorption. The protonation of EB occurs through HCl diffusion within the polymer chains in the PVC/PANI composite. After UV-exposure, the composite turns to green-color, which is related with the emeraldine salt. Contrary to film prepared from THF, a negative coloration is obtained with blends prepared from N-methylpyrrolidine (NMP).

The origin was proposed to be a proton-trapping effect due to solvent traces behaving as usual PVC additives.

Effects of molecular doping by hydroquinone on morphology and optical properties of PANI are studied by U. P. Parkhutic and E. Matveeva [52]. Thin films of the emeraldine base (EB) form of PANI containing different forms of hydroquinones are cast from the solutions of EB/HQ in N-methylpyrrolidinone (NMP). Their properties are studied using optical micrography, UV-Vis, and infrared absorption. It is found that hydroquinones act as molecular dopants of PANI by donating protons from their OH groups to the imine centers of the polymer and thus provoking a conversion of EB toward the emeraldine salt (ES). The extent of this conversion process is determined by the concentration of HQs and their ability to transform into the anion. Other important parameters are the temperature of drying and the time of storage of the liquid substance before casting. Because of the presence of at least two OH groups in HQ molecules, they can react with two or more imine centers of the polymer, thus bringing different polymer chains and changing their ordering. Drying of the macroscopically ordered EB/HQ liquid allows one to fix this ordering and observe the nucleation and the growth of the spherulite crystals. Thus, HQ molecules play a double role in determining the structure and properties of emeraldine base. They, on one hand, produce protonation of the imine bonds of the polymer, similar to the mechanism of acid anion doping, and on the other hand, they operate as agents, causing the reorientation of conformational planes in polymeric chains and their mutual ordering.

Accelerated photodegradation of PVC was studied by Torikai et al. [53]. Accelerated photodegradation of PVC under longwavelength radiation (simulating terrestrial sunlight) by pre-irradiation with shorter wavelengths than terrestrial sunlight is confirmed by molecular weight changes in PVC and absorption spectral analysis. It is found that the threshold wavelength for main-chain scission of PVC shifts to longer wavelength or pre-irradiation. The experimental results confirm that accelerated photodegradation of PVC under terrestrial sunlight is possible by pre-irradiation with shorter wavelength radiation.

Birer et al. [17-19] have studied the UV induced changes in PVC composites by using UV-Vis, IR and XPS. Polyaniline/Poly(viynil chloride) (PANI/PVC) composite in its basic (nonconducting) form and its acidic (conducting) form have been prepared by exposure to gamma-rays or UV radiation. The strong polaron band starting around 600 nm in acidic form is the spectroscopic fingerprint of the electrical conductivity which is very weak and blue shifted in the basic form. The FTIR spectra also verify the increase in the electrical conductivity, as the free carrier absorption band starting around 1600 cm^{-1} develops upon irradiation.

In another study, polyene films containing certain amounts of poly(ethylene glycol) s (PEG) catalyst is extensively dehydrochlorinated by aqueous potassium hydroxide. The molar mass of the PEG used as phase transfer catalyst is ranged from 200 to 800 $gmol^{-1}$. According to the results of elemental analysis and UV-Visible, Fourier Transform-infrared (FT-IR) and FT-Raman spectra, the polyene films obtained from these systems are polyacetylene-like and contain relatively long conjugated sequences. At room temperature the highest conversion is measured to be about 90%. The conductivity of iodine-doped polyene films is found to be as 10^{-2} S cm^{-1} [54].

Agarwal [55] studied the hydroquinone/quinone redox system in the photoyellowing of mechanical pulps. In the area of photoyellowing of mechanical pulps, that HQ/Q redox couple is present in lignin-rich mechanical pulps. It was also noted that compared to a control pulp the concentration of quinones was significantly higher in a photoyellowed pulp. Under ambient conditions, upon exposure to the light, the existent pulp HQs were converted to Qs. To further investigate the importance of HQ/Q redox couple in photoyellowing, studies of methyl-hydroquinones and methyl-quinones carried out. Based on this research, it is shown that the HQ/Q redox system can successfully explain most of the observations related to photoyellowing. Consequently, the HQ/Q redox couple plays a highly significant role in pulp photoyellowing.

The effect of PANI morphology on hydroquinone (HQ)/quinone (Q) redox reaction has been studied by Duic and Grigic [56]. The catalytic effect of PANI on the HQ/Q redox

reaction has been investigated with respect to different morphologies, which are known to depend on the counter-ions during the synthesis. It has been established that PANI lovers the HQ/Q reaction potential difference, ΔE_p, obtained by cyclic voltametry. It is shown that the decrease in ΔE_p doesn't depend on the increase in the thickness of PANI layer, and there is no difference in the case of $PANISO_4$ and PANICl electrode. The increase in the I_p values in the cyclic voltammograms of PANI, compared to Pt electrodes, is explained by the increase in the real surface area of PANI electrodes and the difference in $PANISO_4$ and PANICl morphologies.

Of the previous studies photosensitised dehydrochlorination of PVC by benzophenone is among the most important one. The mechanism of the benzophenone-photosensitized degradation of films of PVC was studied. Absorption of a photon populates a n ➔ π^* singlet state (^1B) which undergoes intersystem crossing with almost 100% efficiency to form triplet benzophenone (^3B). It is supposed in this study that the dehydrochlorination reaction is initiated by abstraction by ^3B of a methylenic hydrogen atom from PVC to form a ketyl radical and a radical derived from PVC. They proposed a mechanism involving chlor radical as the chain propagating species. In this study, Owen and Bailley [10] estimated the length of the polyene sequence formed by HCl elimination to be approximately ten.

A commercial thermal antioxidant has been shown to photosensitize the dehydrochlorination of PVC by Foster et al. [57]. The species responsible is shown to be a p-alkyl-substituted phenol, and this is confirmed using p-cresol as a model compound. Although phenols are commonly used as thermal antioxidants in which capacity they act as radical scavenger, the capacity to act as potent photosensitizer of dehydrochlorination is not expected. This property is confirmed by the use of p-cresol as a model compound, however the mechanism of the process is not explained in this study.

In another study [58] Hirayama et al. have shown the mechanism of sensitized photodehydrochlorination of PVC by using p-cresol as a model compound. A quantitative

study of the effect of chlorinated alkanes upon the fluorescence of p-cresol in solution shows that quenching is due to charge transfer interactions that means the halogenated compound acts as electron acceptor. Because t-butyl chloride does not quench p-cresol fluorescence, it is concluded that the photosensitization occurs via the triplet state of the p-cresol, and this view is confirmed by addition of triplet quenchers. In this work the mechanism is clearly explained, initial exciplex formation being followed by electron transfer.

In another study [59], the humic and fulvic acid extracted from a Ranker type soil sensitize the transformation of monuron. When monuron is irradiated at 365-nm in the presence of the fulvic acid, its degradation is faster in deoxygenated medium than in air-saturated solution. Chloride ions are released, and the para-hydroxylated derivative is formed as upon direct photolysis. It is deduced in this study that the consumption of monuron observed in the absence of oxygen is due to an energy transfer from reactive triplet state of the fulvic acid to monuron. Energy transfer reactions also take place when hydroquinone or acetophenone are used as sensitizers, showing that the energy level of the triplet state of monuron is lower than 311 kJ mol^{-1}.

2. EXPERIMENTAL

2. 1. Preparation of Samples

Poly(vinyl chloride) was purchased from Aldrich and was used without further purification. Three different PVC having inherent viscosities 0.92 (Mn=55 000 and Mw=97 000), 1.02 (Mn=60 000 and Mw=106 000) and 1.40 (Mn=99 000 and Mw=233 000). The films were prepared by casting the solutions on glass (or quartz). In order to achieve homogeneous films long (3-4 hours) dissolution and casting times were employed.

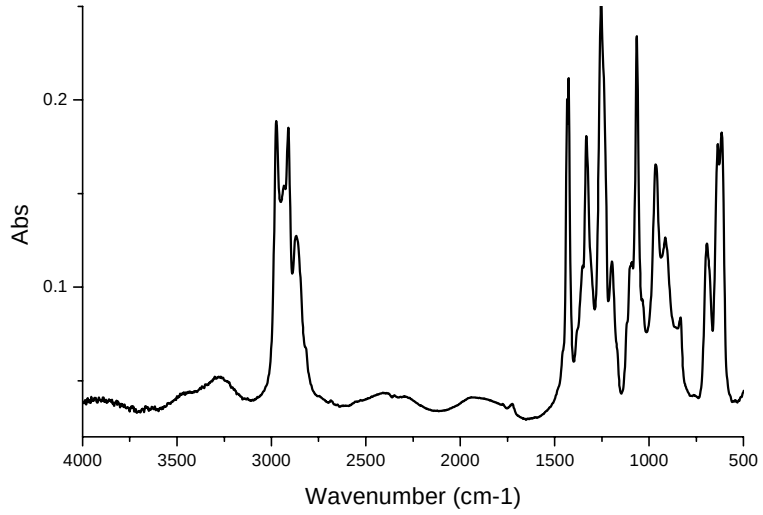


Figure 6: FTIR spectrum of PVC.

The FTIR spectrum of PVC is given in Figure 6. The spectrum of PVC does not indicate any significant quantity of impurity that should be considered carefully. The bands at 2970 cm^{-1} and 2912 cm^{-1} are result from the C-H stretching of CHCl and C-H stretching of CH_2, respectively. A very small band at 1718 cm^{-1} indicates the presence of carbonyl (which in most cases is unavoidable) resulting from the impurities coming from the polymerization. At 1435 cm^{-1}, one can easily see the CH_2 deformation. Also C-H

deformation of H-C-Cl can be seen at 1331 cm^{-1}. At 1099 cm^{-1} there is a strong peak due to C-C stretching. 966 cm^{-1} shows the CH_2 rocking. Finally, there is a strong peak of C-Cl stretching at 600-700 cm^{-1}. Figure 7 shows the UV-Vis spectrum of PVC. The spectrum

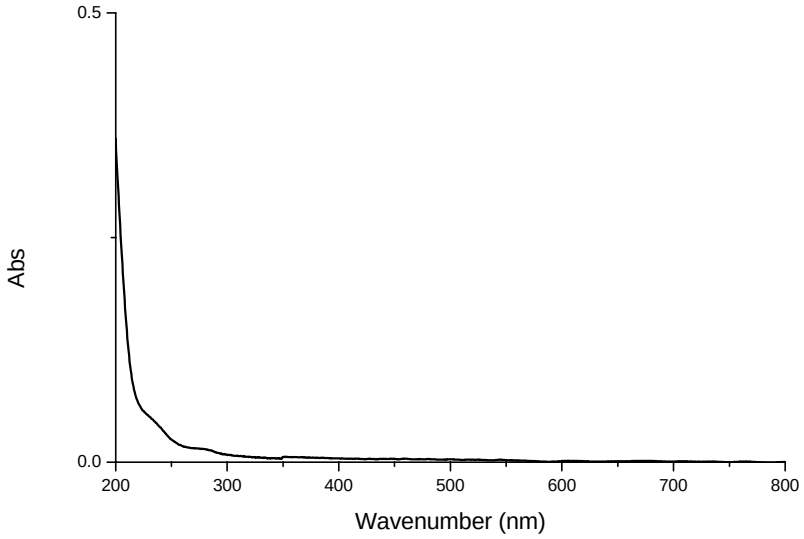


Figure 7: UV-Vis spectrum of pure PVC.

does not indicate presence of any light absorbing groups above 250-nm [60].

Methyl violet (MV) and polyaniline (PANI-emeraldine base) are purchased from Aldrich and used without further purification. The FTIR spectra of basic and salt form of PANI are given in Figure 8. The change in the intensity of 1600 cm^{-1} and 1500cm^{-1} peaks show the protonation of the imine nitrogens. In this transformation the insulating base (EB) form is converted to the conducting salt (ES) form. Assignment of the bands is summarized below.

1. 3500-3100 cm^{-1}

This is the N-H stretching region. The absorption of PANI in this region is rather weak. The main absorption peaks are located at 3380 and 3310 cm^{-1}. After treatment with HCl, the peak at 3380 cm^{-1} increases and the shoulder at 3170 cm^{-1}decreases. So it is possible to assign 3460 and 3380 cm^{-1} to asymmetrical and symmetrical stretching vibrations of NH_2, 3380 cm^{-1} to N-H stretching in B-NH-B, the broad band at 3310 cm^{-1} to hydrogen bonded NH and 3170 cm^{-1} to terminal Q=NH.

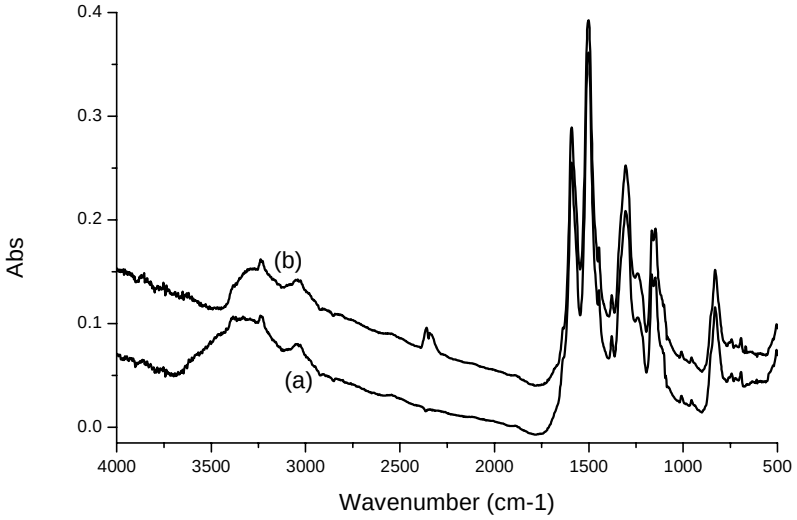


Figure 8: FTIR spectra of PANI base (a) salt (b).

2. 3100-2800 cm^{-1}

This is the C-H stretching region. The absorption of PANI in this region is even weaker, but is observable at 3050-3030 $cm^{-1}$and 2960-2850 cm^{-1}. Upon the treatment with HCl, the relative intensity of the 3040 cm^{-1} peak decreases, indicating that the number of H atoms bonded to the benzene ring is reduced [23-28].

3. 1600-1450 cm^{-1}

Aromatic ring, N-H deformation and C=N stretching give absorptions in this region. The band at 1510 $cm^{-1}$is mainly due to the benzenoid ring (B) stretching in PANI. A band near 1587 cm^{-1} is related to quinoid (Q) structure in PANI. Upon addition of HCl, the relative intensity of 1587 to 1510 cm^{-1} decreases. The conductivity of PANI products

obtained after HCl addition decreases in the same order. With the above assignments, this might be explained as the decrease in Q/B.

4. 1400-1240 cm^{-1}

This is the C-N stretching for aromatic amines. The intrinsic PANI shows three peaks: medium absorption at 1315 cm^{-1} and weak ones at 1380 $cm^{-1}$and 1240 cm^{-1}.

5. 1220-500 cm^{-1}

This is the region of in-plane and out-of-plane bending of C-H bonds on aromatic rings. The main absorption bands for intrinsic PANI are located at 1160 cm^{-1} and 830 cm^{-1}. Substitutions can be seen from the assignments. 1220, 1105, 1010 and 830 cm^{-1} stand for 1,4-substitution, 1115, 1060, 960, 995 and 850 cm^{-1} for 1,2,4-substitution and 740 and 690 cm^{-1} for 1,2-or mono-substitution. 810 cm^{-1} corresponds to C-Cl stretching [61].

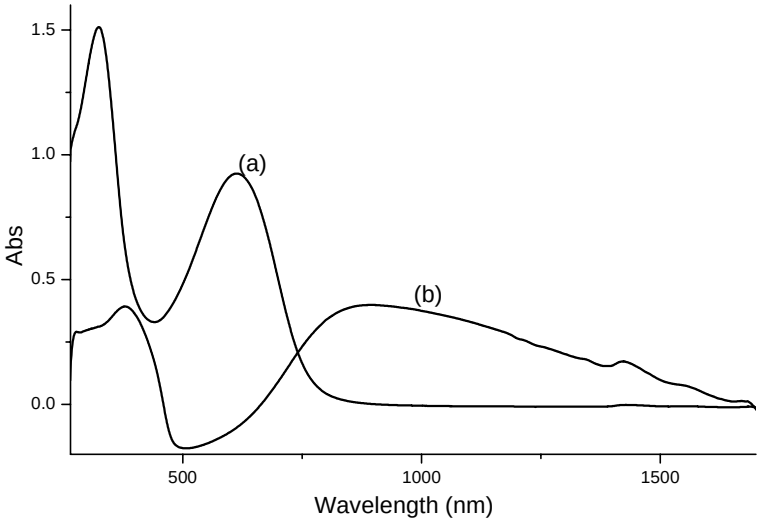


Figure 9: UV-Vis-NIR spectra of PANI base (a) and salt (b).

The structural change caused by the addition of HCl can be monitored by UV-Vis-NIR spectroscopy. The salt form of PANI has a large polaron band, however the base form does not have any absorption in that region (1220-500 cm^{-1}). Figure 9 shows the insulating and conducting form of PANI. All of the samples are prepared by dissolving the components in distilled THF. Composition of each system is indicated for the specific

samples. The solutions are cast onto glass slides and the freestanding films are peeled off from them afterwards. After formation of uniform films, UV-Vis-NIR and FTIR spectroscopic investigations are done. The average thicknesses of the films are of the order of several micrometers (measured). Tetrahydrofuran (THF) is from Carlo Erba. THF contains 0.05% hydroquinone to prevent peroxide formation. THF is double distilled in the presence of KOH to remove the impurities and hydroquinone.

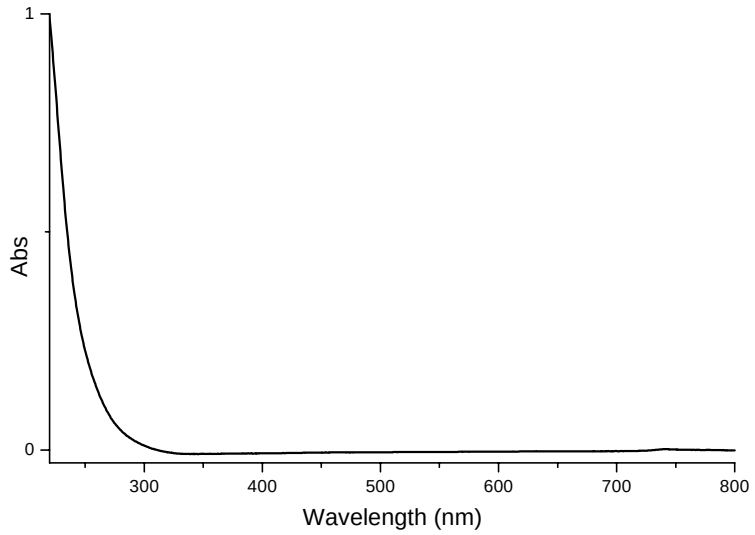


Figure 10: UV-Vis spectrum of THF.

Figure 10 shows the UV-Vis spectrum of the THF and it does not indicate any light absorbing groups (chromophores or impurities) above 300 nm.

Figure 11 shows the IR spectrum of the THF. The spectrum shows three main peaks. At about 2900 cm^{-1}, there are two kinds of C-H stretching, one is near the oxygen atom and another is far away from the oxygen atom in the THF molecule. Others are C-C stretching at 1100 cm^{-1} and C-O stretching at 950 cm^{-1}. Also there is a small peak of C-H deformation at 1435 cm^{-1}.

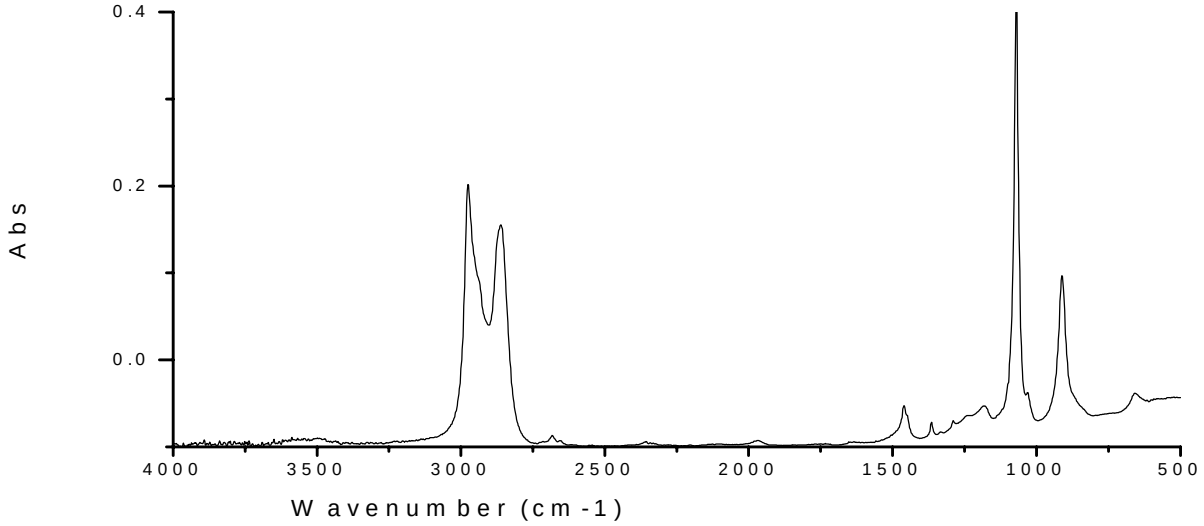


Figure 11: IR spectrum of THF.

2. 2. Irradiation Studies

Irradiation studies are carried out with a low-pressure mercury lamp (7mW/cm^2) emitting a single line at 254 nm and a low-pressure fluorescent filter coated lamp (8mW/cm^2), that emits mostly at 312 nm.

2. 3. Temperature Studies

In this part, the experiments are performed at two different temperatures 0 and 20 C^0. The lamps are suited in a special cold room that the temperature of the room is kept constant. After the irradiation is completed, the samples are put in the UV-Vis spectrophotometer to. All spectra are taken at room temperature.

2. 4. Flux Studies

Flux of the irradiation is adjusted for each of the experiment by changing the position of the lamp from the ground. All the measurements are done at room temperature. Only the distance of the irradiation is changed for the desired experiments. Effect of the distance on the photodegradation is measured by taking the UV-Vis spectra of the desired samples.

2. 5. UV-Vis Spectroscopic Studies

The UV-Vis Spectra of the samples are recorded with a Varian Cary 5 Spectrophotometer. Cary 5 is a double beam spectrophotometer. The instrument is equipped with interchangeable deuterium/tungsten sources, a reflection grating monochromator, and a photomultiplier detector. The beam splitter is a motor driven circular disk or chopper that is divided into three segments, one of which is transparent, the second reflecting, and the third opaque. With each rotation, the detector receives three signals, the first corresponding to P_0, the second to P, and third to the dark current. The resulting electrical signals are then processed electronically to give the transmittance or absorbance on a readout device. Double beam instruments have the advantage that they compensate for all but the most short-term fluctuations in the radiant-output of the source as well as for drift in the detector and amplifier. They also compensate for the wide variations in source intensity with wavelength. Furthermore, the double beam design lends itself to the continuous recording of transmittance or absorbance spectra [33].

The samples irradiated with 254 nm and 312 nm lamps are put in the spectrometer following the irradiation and their spectra are recorded with 300 nm/min speed and 2 nm spectral band width.

2. 6. FTIR Studies

The IR spectra of the samples are recorded with a Bomen Hartman MB-102 model FTIR spectrometer. The spectra are taken with the total number of scans 32 and a resolution of 4 cm^{-1}.

2. 7. XPS Studies

To record the XPS spectra a Kratos ES 300 electron spectrometer, equipped with a MgKα source of 1253,6 eV, is used.

3. RESULTS

3. 1. Photodegradation

3. 1. 1. Degradation at 254 nm

The photodehydrochlorination is the most important photochemical reactions that occur in PVC under UV irradiation. It also leads to the formation of polyene segments with different number of conjugated double bonds. The presence of these polyenes in polymer chains is responsible for coloration of PVC. The most important consequence of exposure

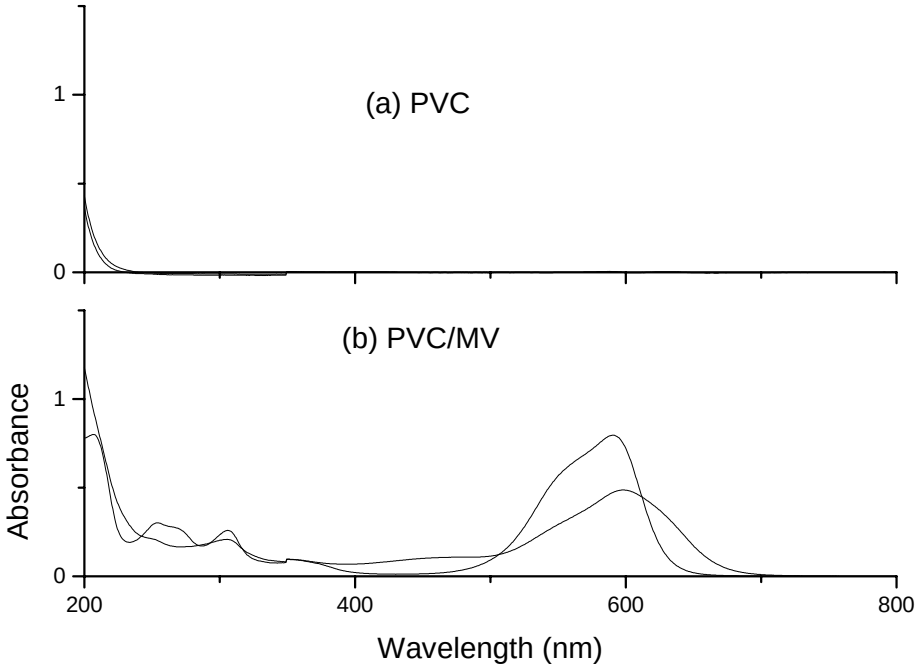


Figure 12: UV-Vis spectra of (a) PVC and (b) PVC/MV exposed to 254 nm irradiation for 30 minutes.

of PVC to UV is the light-induced yellowing phenomenon. Whereas the pure polymer doesn't absorb ultraviolet radiation greater than 250 nm, the polymer containing significant concentration of chromophores is able to do so. Absorption of light results in "zip" dehydrochlorination of the polymer leading to the formation of conjugated polyene

sequences. Longer polyene sequences are able to absorb longer wavelengths of light and consequently lead to further dehydrochlorination of the polymer resulting in the formation of conjugated polyene sequences. When the sequence length exceeds about 5-8 units, polyenes absorb blue light, which results in yellowing of the material [1].

At 254 nm, PVC dehydrochlorination starts with the cleavage of carbon-chlorine bond and further abstraction of an adjacent hydrogen. In pure PVC the dehydrochlorination process can be indirectly monitored using UV-Vis Spectroscopy. Figure 14a shows the UV-Vis spectrum of the PVC irradiated at 254 nm for 30 minutes. A small amount of polyene formation (within 30 minutes) can be observed which demonstrates the dehydrochlorination of PVC at this wavelength. However, a direct proof requires monitoring the HCl generated for which an indicator is mostly suited. Figure 12b shows the spectrum of PVC/MV irradiated at 254 nm. The spectrum indicates a decrease in the MV peak at 600 nm because of the HCl photogenerated from the PVC at this wavelength.

3. 1. 2. Degradation at 312 nm

Pure PVC does not absorb at 312 nm to lead to significant dehydrochlorination as demonstrated in Figure 13. Figure 13a shows the spectrum of PVC irradiated for 30 minutes. The spectrum does not indicate presence of polyenes formed. Keeping in mind that HCl detection by MV is more sensitive we have also followed this process in the presence of MV. As shown in Figure 13b, 312 nm irradiation of pure PVC does not lead to significant HCl generation.

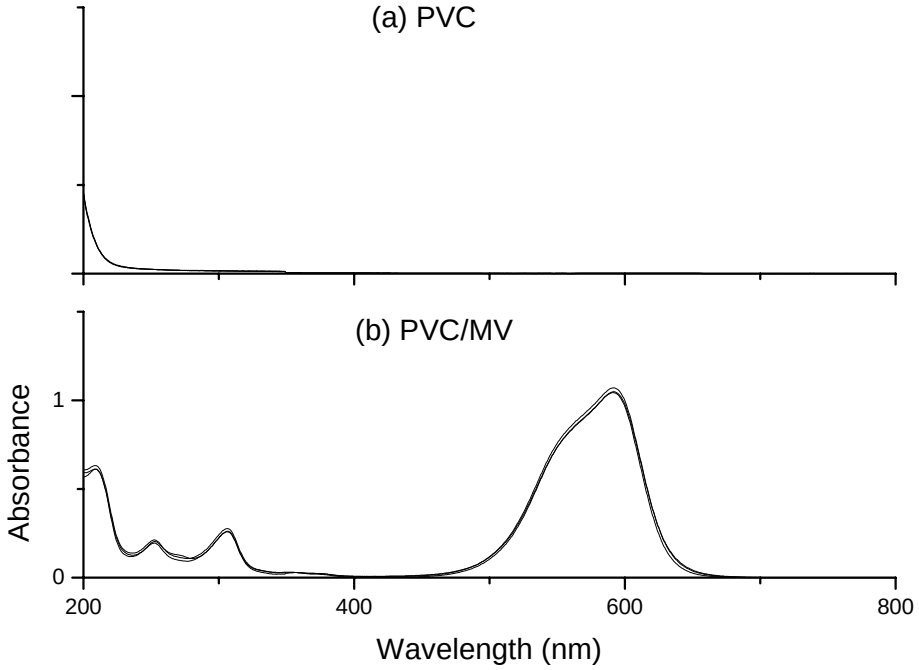


Figure 13: UV-Vis spectra of (a) PVC and (b) PVC/MV irradiated at 312 nm for 30 minutes.

3. 2. Photosensitization by Hydroquinone

As it is shown in Figure 14, PVC dehydrochlorinates significantly when exposed to the 312 nm UV light in the presence of hydroquinone [20]. Without HQ there is no significant dehydrochlorination of PVC at 312 nm as shown in the Figure 13. Since the main aim of this study is a deeper understanding of this sensitization by HQ various factors like flux of the photon source, concentration of HQ, temperature, and intrinsic viscosity/molecular weight of PVC are investigated in detail using the change in MV absorption at 590 nm [17-19]. Furthermore, XPS and FTIR spectroscopic methods are also applied to follow the dehydrochlorination process at 312 nm.

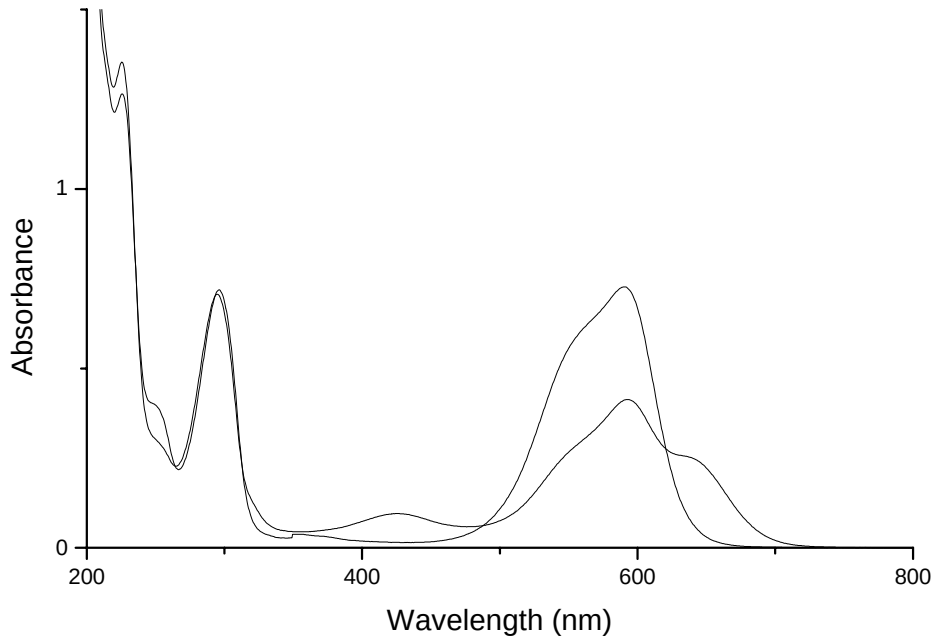


Figure 14: UV-Vis spectra of PVC/HQ/MV blend irradiated at 312 nm for 60 minutes.

3. 2. 1. Concentration Dependence

Concentration of the HQ in the matrix of the sample is an important parameter that strongly affects the rate of the photodehydrochlorination. Effective HQ concentration for the start of the degradation is determined by changing the mass concentration (w/w) of the HQ. Figure 15b demonstrates the UV-Vis spectra of HQ-PVC blends irradiated at 312 nm for 30 minutes. As shown in Figure 15a HQ assisted degradation of PVC has a well-defined HQ concentration threshold in the matrix of the blend.

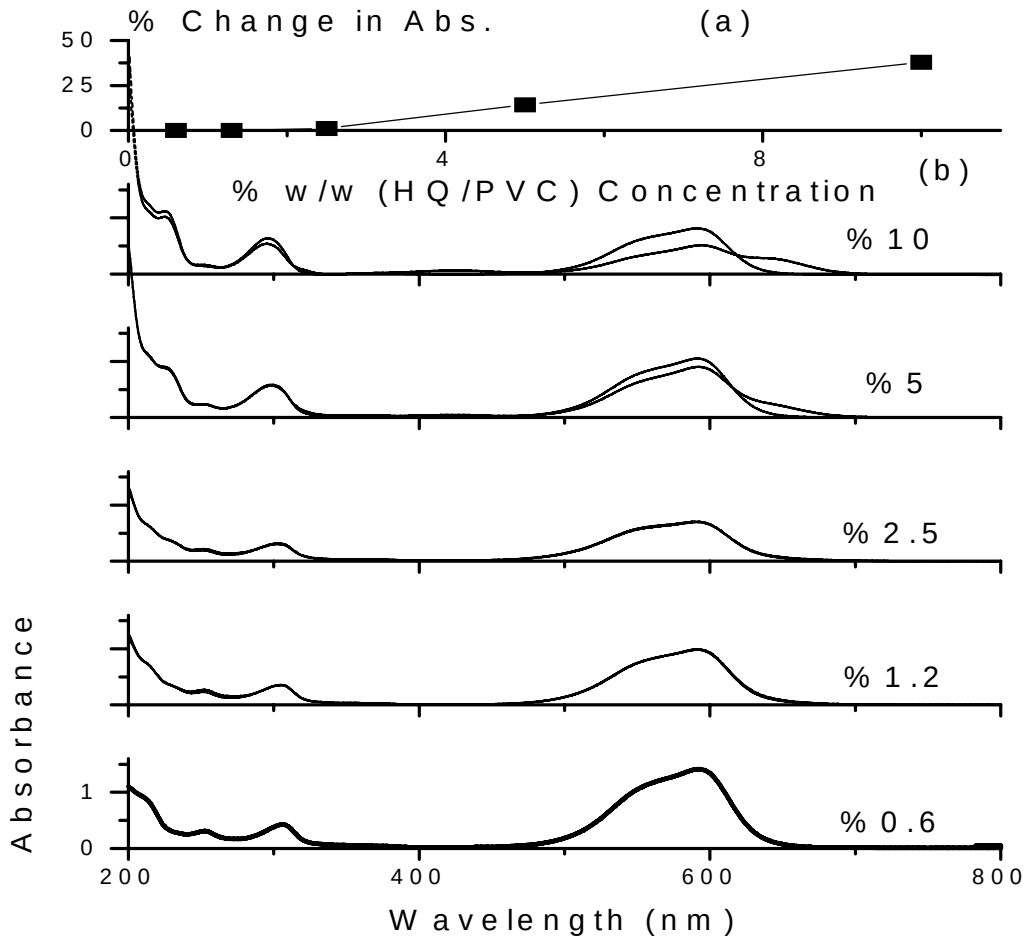


Figure 15: Graph of % change in absorbance of MV with the concentration of HQ (a) and UV-Vis spectra of PVC/HQ/MV irradiated at 312 nm for 30 minutes at different mass concentration of PVC: HQ (b).

3. 2. 2. Flux Dependence

In this part of the work, flux (number of incoming photons per unit area) of the irradiation at 312 nm is investigated. Since our radiation source is not a point source but distributed to a 10 cm x 20 cm area, we assume that the flux is inversely proportional to the distance of the irradiation. For each of the experiment, we chose a 5 cm increase in the distance of the irradiation as shown in Figure 16b. Figure 16a shows the % change in the MV absorption at 590 nm after irradiation at 312 nm for 30 minutes with respect to the distance from the source (assuming inverse proportionality with the flux of the

irradiation). As the flux of the irradiation increases the percent change in the absorption of the MV increases.

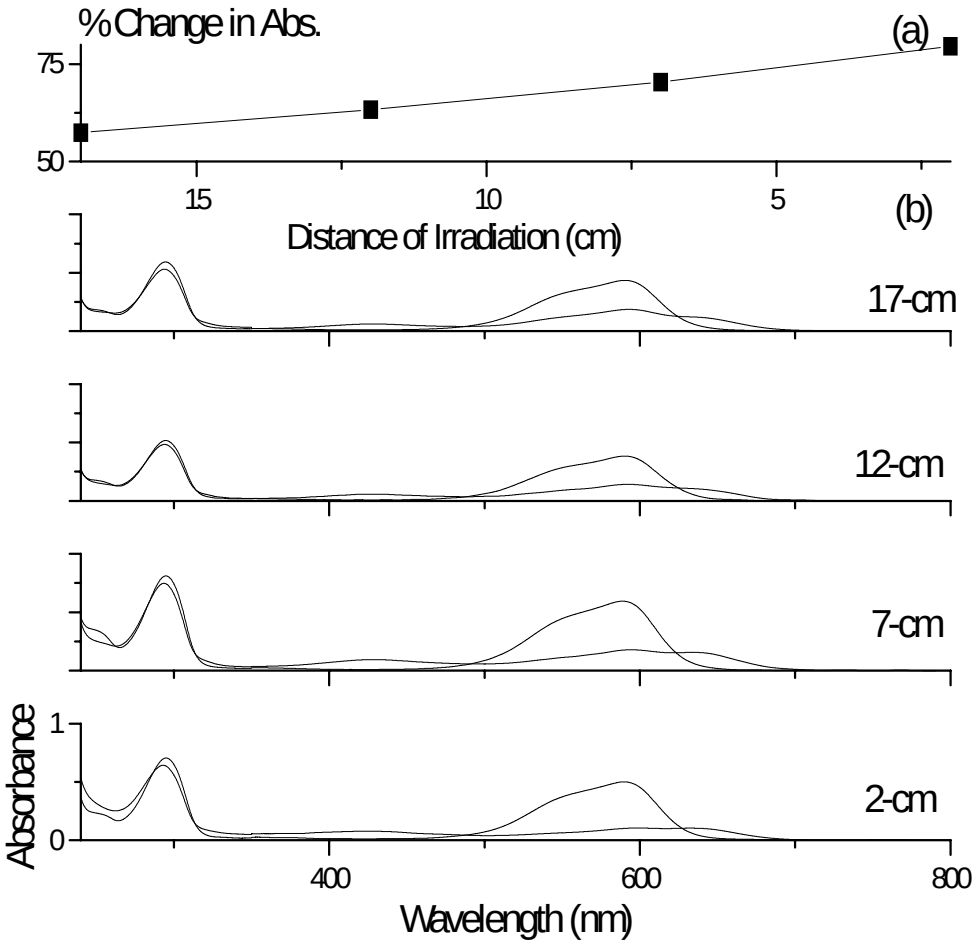


Figure 16: Graph of % change in absorbance of MV with irradiation distances (a) and UV-Vis spectra of the PVC/HQ/MV blend irradiated at 312 nm for 30 minutes from 2-cm, 7-cm, 12-cm, 17-cm (b).

Thus we can conclude that HQ assisted PVC degradation depends linearly on the number of photons incoming to the surface of the blend (i. e. no non-linear effects are obvious).

3. 2. 3. Temperature Dependence

Temperature of the medium is also a key parameter that effects the rate of the HQ assisted photodehydrochlorination of PVC at 312 nm. In order to explore the effect of the temperature on the rate of photodegradation, experiments were performed at two different temperatures. Figure 17b through 17e demonstrates the effect of temperature on the rate of photodehydrochlorination. Figure 17a depicts the results. Using Arrhenious equation,

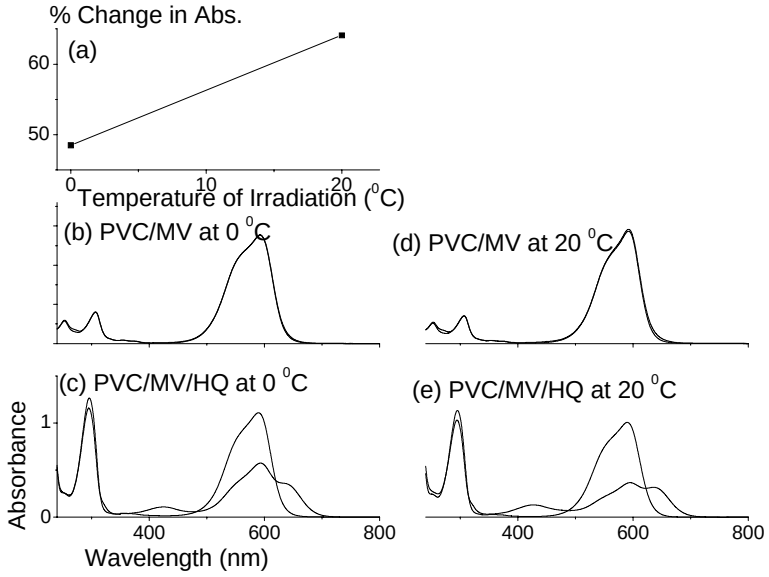


Figure 17: Graph of % change in absorbance of MV at 590 nm with temperature of the irradiation (a) and UV-Vis spectra of PVC/MV and PVC/MV/HQ at 0 and 20 ^{0}C (b-d).

activation energy is calculated to be as 10 kJ/mol. It shows that temperature causes physical change during irradiation, like increase of diffusion as the temperature increases, not a chemical change since chemical reactions activation energy is on the order of 100 and 200 kJ/mol.

3. 2. 4. Intrinsic Viscosity/Molecular Weight Dependence

In order to find the effect of intrinsic viscosity on the hydroquinone assisted photodehydrochlorination of PVC at 312 nm, PVC having different intrinsic viscosities used to make blends with MV and HQ at the desired compositions. Percentage change in the absorbance of MV at 590-nm can show the rate of photodehydrochlorination at the indicated matrix. Figure 18b through 18d show the UV-Vis spectra of the samples having different intrinsic viscosities before and after the irradiation at 312 nm for 30 minutes. Figure 18a shows the percentage change in absorbance of MV at 590-nm for the indicated samples having different intrinsic viscosities. As shown in the Figure 18a the rate of photodehydrochlorination of PVC at 312 nm is inversely proportional to the intrinsic viscosity of PVC.

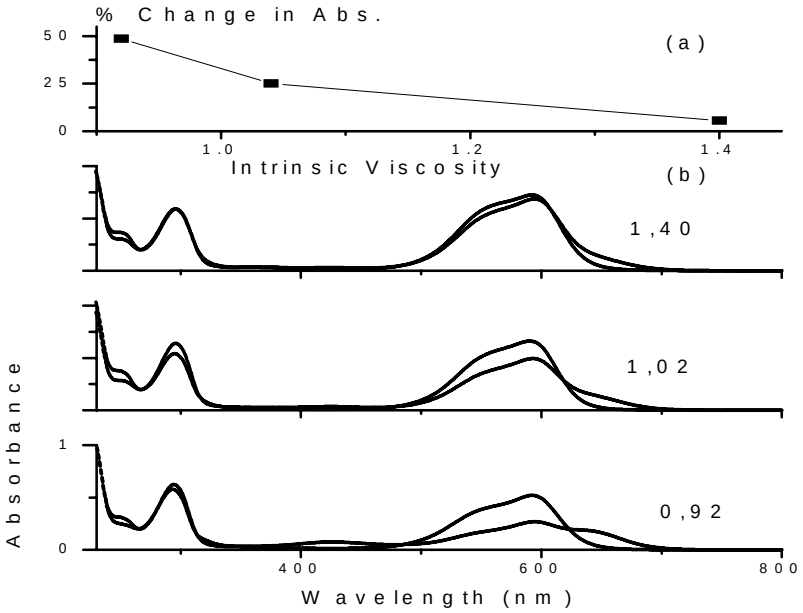


Figure 18: The graph of percentage change in absorbance of MV at 590-nm with respect to the change in the intrinsic viscosities of the sample for 60 minutes (a) and UV-Vis spectra of PVC/MV/HQ at different intrinsic viscosities irradiated at 312 nm (b-d).

3. 2. 5. Hydroquinone-Benzoquinone Dependence

In this part of the work, HQ/BQ composition effect on the rate of photodehydrochlorination is investigated. For this purpose HQ percent mass composition is changed from 0 to 100. During the photodehydrochlorination some of the BQ are converted to the HQ and this can be observed from Figure 19b-19e. The BQ sample that

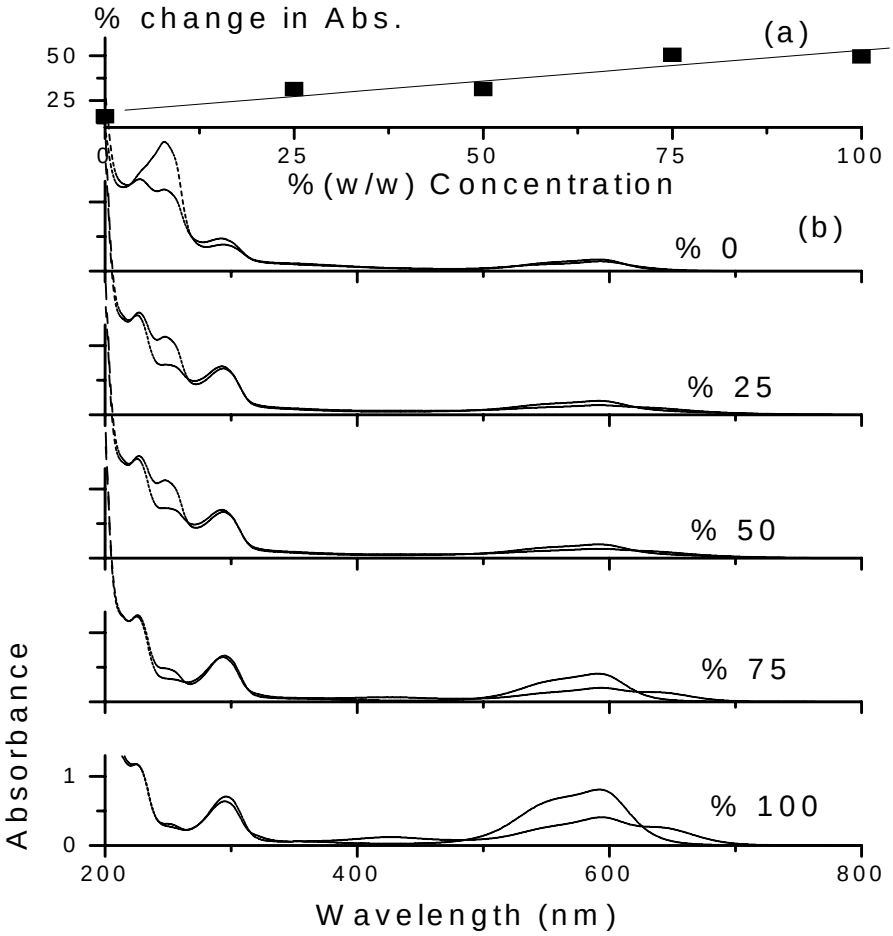


Figure 19: Graph of percentage changes in absorbance of MV at 590-nm for each of the HQ/BQ composition of the sample (a) and UV-Vis spectra of PVC/MV and HQ/BQ having different compositions irradiated at 312 nm for 30 minutes (b-f).

is used in this experiment contains some HQ impurity. Hence, even the pure BQ (%0 HQ) sample shows photodehydrochlorination in this experiment because of the HQ impurity in the BQ sample. Figure 19b through 19f show the UV-Vis spectra of PVC/MV

and different concentration of BQ/HQ couple irradiated at 312 nm. The spectra in Figure 19 indicate that BQ has no effect on the photodehydrochlorination of PVC at 312 nm whereas HQ plays an important role in the photodehydrochlorination of PVC at 312 nm.

3. 3. XPS Investigation of HQ Assisted Photodegradation

In this part of the thesis dehydrochlorination of PVC at 254 nm and 312 nm is investigated by using XPS. In the XPS spectra following peaks are used to monitor the dehydrochlorination of PVC. The peaks at 200eV and 272 eV correspond to the Cl 2p and Cl 2s respectively, which can be used to follow the chlorine content of the blend. The peak at 285eV corresponds to the C 1s [37]. Accordingly ratio of the intensities of C 1s to Cl 2p (more intense than the Cl 2s) can be calculated from the peak areas.

We should note that acquisition of a satisfactory (with good signal-to-noise ratio) XPS spectrum requires 60-120 minutes during which the sample is constantly exposed to X-rays causing dehydrochlorination as well. Therefore, special care must be exercised to differentiate between dehydrochlorination of the sample before and during XPS data recording, Figure 20 shows the XPS spectra of PVC/HQ blends before and after irradiation at 312 nm for 120 minutes and also the effect of x-Ray exposure. The intensity ratio of C 1s to Cl 2p is found to be 0.75 before irradiation at 312nm and 0.73 after the irradiation at 312nm. This result indicates that there is some elimination of HCl after irradiation at 312 nm. However, after the X-ray irradiation of the sample, there is a larger change, 0.75 to 0.56 for the sample not exposed to UV and from 0.73 to 0.62 for the sample, which was exposed to 312 nm UV light. The X-ray induced dehydrochlorination is much more effective than the UV induced dehydrochlorination. Although XPS gives some indication that there is dehydrochlorination of PVC, it cannot be used to follow the dehydrochlorination reliably.

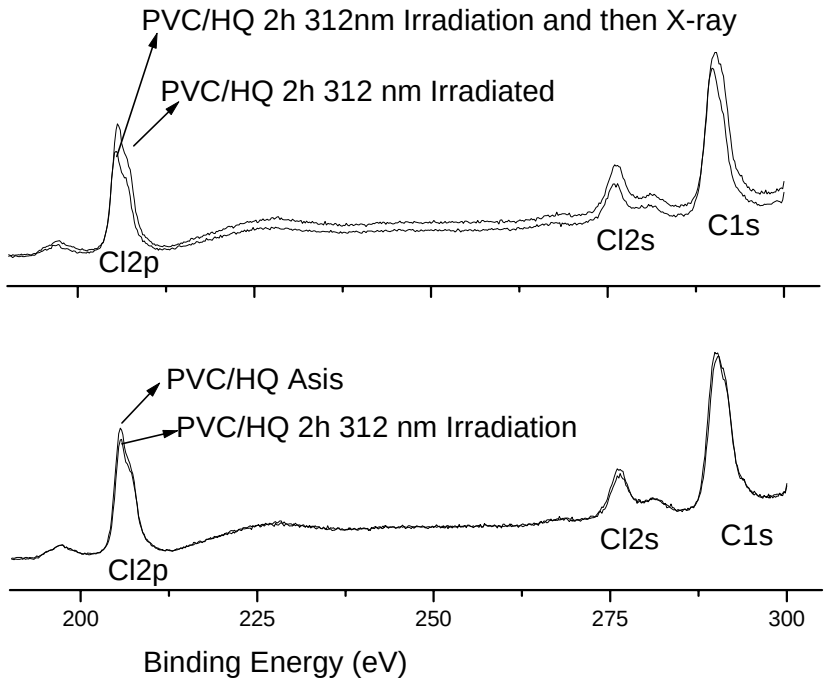


Figure 20: XPS spectra of PVC/HQ blends irradiated at 312 nm for 120 minutes.

3. 4. FTIR Investigation of HQ Assisted Photodegradation

FTIR is an important spectroscopic technique that can be used to elucidate the major chemical changes during the irradiation of the PVC blends. In this case the peaks at 3300-3500 cm^{-1} corresponding to O-H stretching, 1600-1700 cm^{-1} corresponding to C=O stretching, 2900-3000 corresponding to C-H stretching, 600-700 cm^{-1} corresponding to C-Cl stretching and 3000-3080 aromatic C-H stretching are some of the peaks that could be taken into account for the analysing degradation of PVC at different wavelengths [62].

3. 4. 1. Photodegradation at 254 nm

Since almost all polymeric materials (including PVC) absorb UV at 254 nm, severe degradation at this wavelength is expected [8]. Figure 21 shows the IR spectra of PVC (a) and PVC/HQ (b) irradiated at 254 nm for 60 minutes. The major indication of

degradation is the formation of carbonyls after irradiation for both PVC and PVC/HQ blends. There are also minor changes in the C-H and O-H stretching of the samples but no significant change in the C-Cl peaks could be detected.

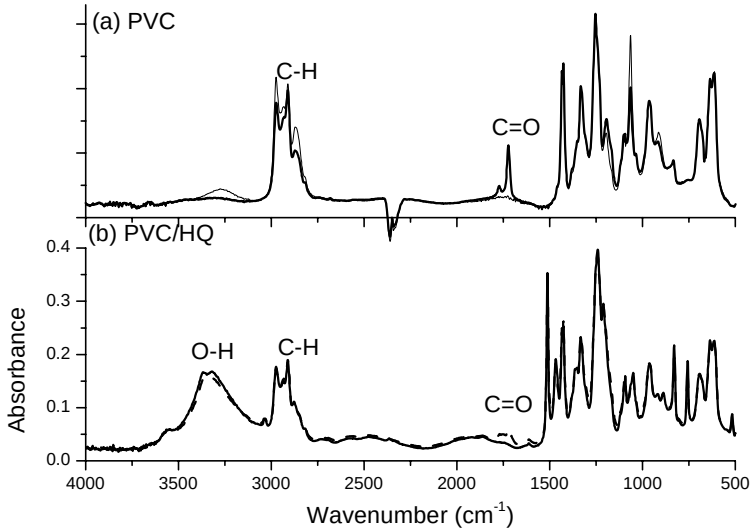


Figure 21: IR spectra of PVC (a) and PVC/HQ (b) irradiated at 254 nm for 60 minutes.

3. 4. 2. Photodegradation at 312 nm

Photodegradation at this wavelength is the key phenomenon for the understanding of sensitization by HQ. Figure 22 shows the IR spectra of PVC (a) and PVC/HQ (b) before and after the irradiation for 60 minutes at 312 nm. Carbonyls are formed in PVC/HQ and there is very little decrease in O-H stretching after irradiation. In the case of PVC there are neither significant changes in the C-H stretching nor in the carbonyl region.

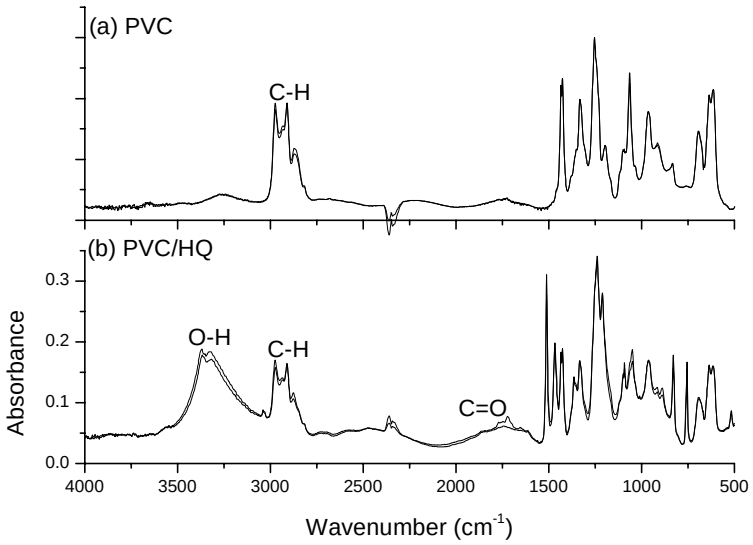


Figure 22: IR spectra of PVC (a) and PVC/HQ (b) irradiated at 312 nm for 60 minutes.

In order to observe the long time effects of UV irradiation at 254 nm and 312 nm, different films of PVC are used. Figure 23 shows the 12 hours-exposed films of PVC at 254 and 312 nm. It is clear from the spectra that 254 and 312 nm UV irradiation of pure PVC don not show a change in the C-Cl stretching, however 254 and 312 nm UV irradiation of PVC/HQ show a decrease in the C-Cl stretching. By following C-Cl stretching, it is certain that HQ has strong effect on the rate of dehydrochlorination. After long time exposure to 254 and 312 nm UV radiation, carbonyl formation is detected but this is not crucial observation to be taken into account since all the samples show nearly the same amount of carbonyl formation.

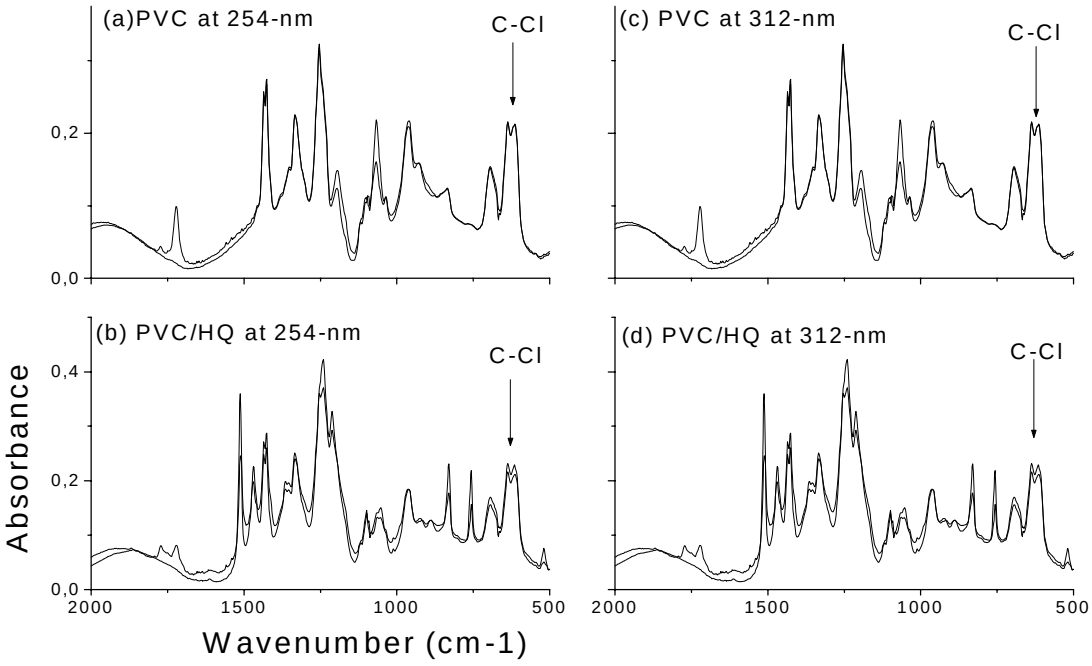


Figure 23: IR spectra of PVC and PVC/HQ at 254 and 312 nm before and after 12 hours.

3. 5. Sensitization

In this section, comparison of HQ with similar compounds in terms of their photochemical sensitization ability for the blends of PVC/MV irradiated at 312 nm will be reported. Ability of the sensitizers will be quantified using the percentage change in the absorbance of MV at 590-nm after irradiation at 312 nm for 30 minutes. Behavior of hydroquinone and benzoquinone was already explained in the previous sections.

3. 5. 1. Phenol

Phenol is similar in structure to the HQ, however with only one –OH group. As can be inferred from the Figure 24, 312 nm UV light has no effect on the PVC/phenol/MV sample, probably due to the absence of any absorption around this wavelength. Figure 24

shows the UV-Vis spectra of phenol (a) and PVC/phenol/MV irradiated at 312 nm for 30 minutes.

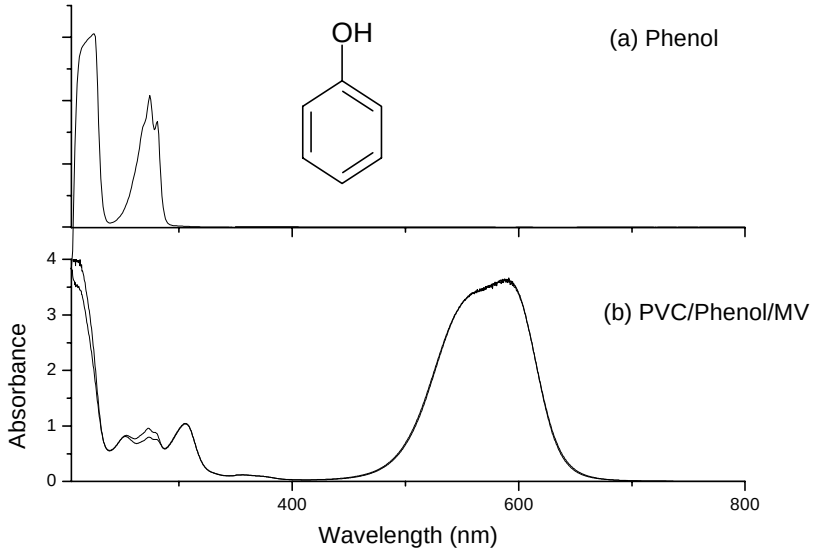


Figure 24: UV-Vis spectra of phenol (a) and PVC/phenol/MV irradiated at 312 nm for 30 minutes.

3. 5. 2. 1,3,5-Trihydroxybenzene

Although it has three hydroxyl groups this compound has not affected the photodegradation of PVC at 312 nm either. The change in the absorbance of MV is little. The structure of this compound is very similar to the structure of HQ but there is no OH groups attached to the para-position. From the experimental result of this compound one can observe that OH groups attached to the para position in HQ have an important role in the photodegradation of PVC. Figure 25 shows the UV-Vis spectra of 1,3,5-trihydroxybenzene (a) and PVC/1,3,5-trihydroxybenzene/MV irradiated at 312 nm for 30 minutes (b).

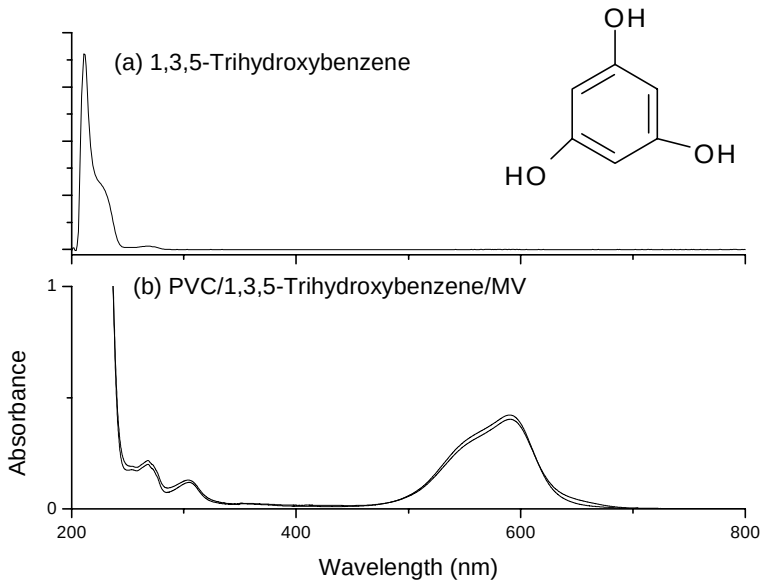


Figure 25: UV-Vis spectra of 1,3,5-trihydroxybenzene (a) and PVC/1,3,5-trihydroxybenze/MV irradiated at 312 nm for 30 minutes.

3. 5. 3. 1-Naphtol

1-Naphtol is similar to the phenol in its structure but 1-naphtol has one difference by having absorbance at 312 nm. Figure 26 shows the UV-Vis spectra of 1-naphtol (a) and PVC/1-naphtol/MV irradiated at 312 nm for 30 minutes. However, it is observed that having absorbance at 312 nm is not the only requirement to initiate photodegradation at this wavelength.

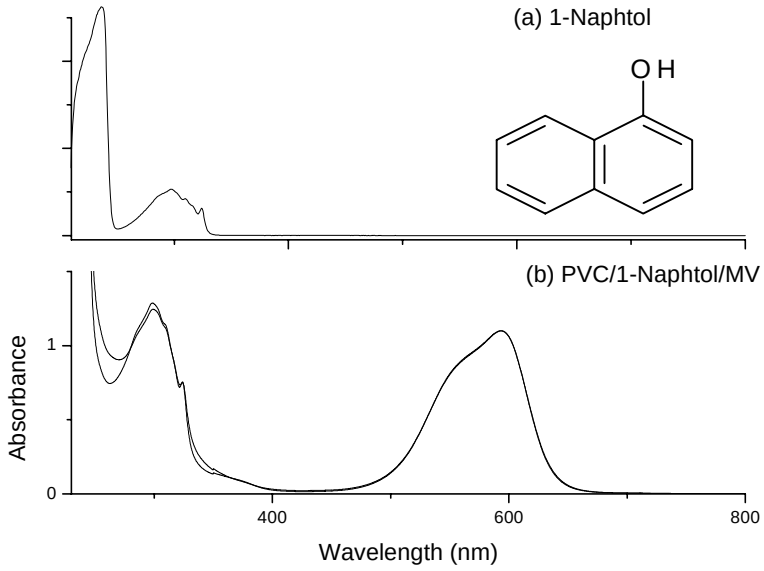


Figure 26: UV-Vis spectra of 1-naphtol (a) and PVC/1-naphtol/MV irradiated at 312 nm for 30 minutes.

3. 5. 4. 4-Hydroxybenzoic Acid

Figure 27 shows the UV-Vis spectra of 4-hydroxybenzoic acid (a) and PVC/4-hydroxybenzoic acid/MV irradiated at 312 nm for 30 minutes. Again, 4-hydroxybenzoic acid shows nearly no effect on the PVC photodegradation. The structure of the compound is very similar to the HQ, having –COOH instead of –OH, in the para position. Although the UV-Vis spectra of HQ and 4-hydroxybenzoic acid are similar, their photochemical behaviors in the blends of PVC are very different.

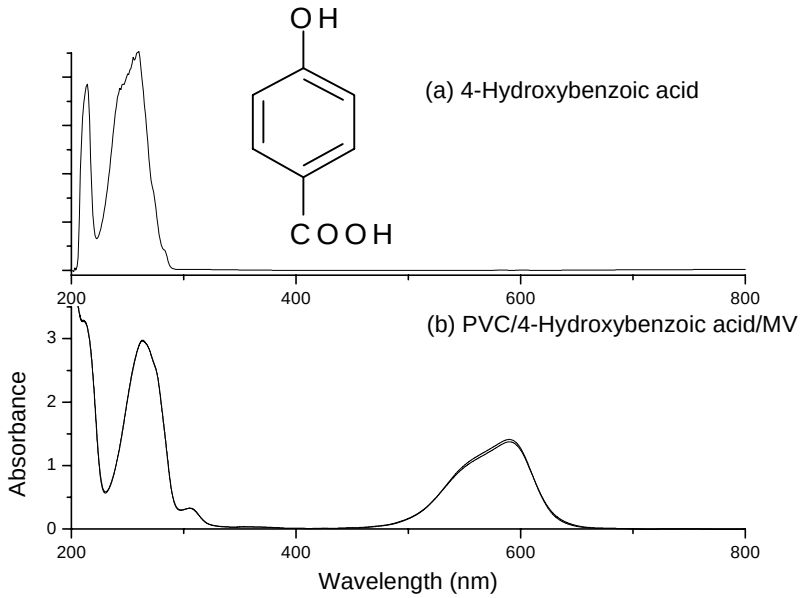


Figure 27: UV-Vis spectra of 4-hydroxybenzoic acid (a) and PVC/4-hydroxybenzoic acid/MV irradiated at 312 nm for 30 minutes.

3. 5. 5. Benzophenone

Of the reported compounds in our study benzophenone is among the most important one since its degradation ability of PVC has already been reported. Owen and Bailley [10] studied the mechanism of the benzophenone-assisted photodegradation of PVC. They claimed that absorption of a photon in the UV region populates a n ➔ π^* singlet state (^{1}B) which undergoes intersystem crossing with almost 100% efficiency to form triplet benzophenone (^{3}B). It was postulated that the dehydrochlorination reaction was initiated by abstraction by ^{3}B of a methylenic hydrogen atom from PVC to form a ketyl radical and a radical derived from PVC. They also proposed a mechanism involving chlorine radical as the chain propagating species. Figure 28 displays the UV-Vis spectra of benzophenone (a) and PVC/benzophenone/MV (b) irradiated at 312 nm for 30 minutes demonstrating its photosensitization ability.

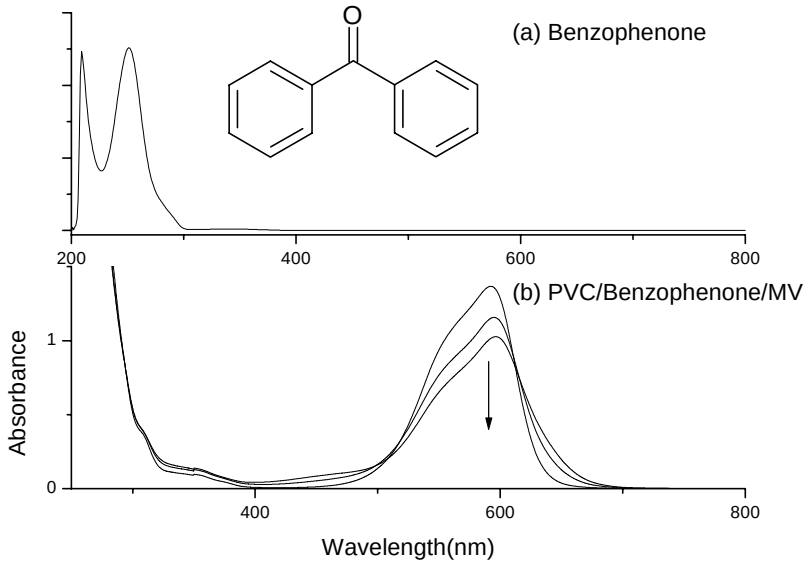


Figure 28: UV-Vis spectra of benzophenone (a) and PVC/benzophenone/MV irradiated at 312 nm for each 30 minutes (b).

3. 5. 6. 2-Acetonaphtanone

Figure 29 shows the UV-Vis spectra of 2-acetonaphtanone (a) and PVC/2-acetonaphtanone/MV irradiated at 312 nm for 30 minutes. 2-acetonaphtanone causes a change of %8.6 of MV absorbance after irradiation, however it is not as effective as HQ.

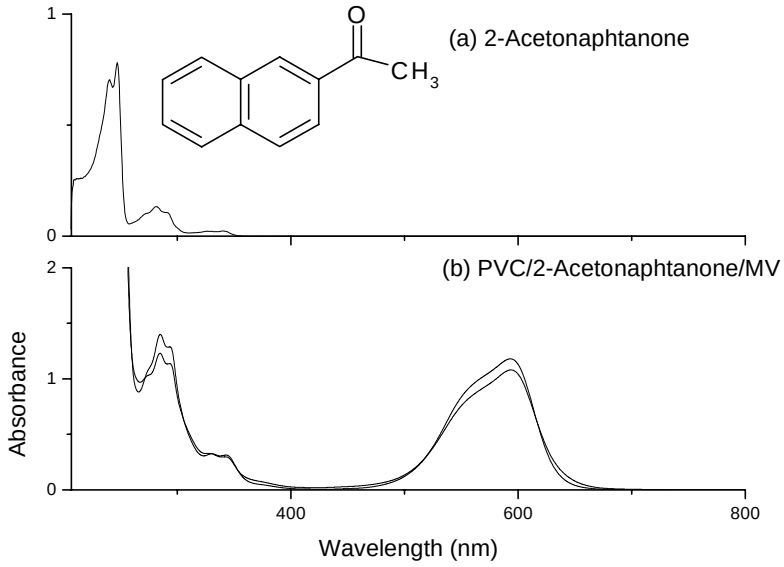


Figure 29:UV-Vis spectra of 2-acetonaphtanone (a) and PVC/2-acetonaphtanone/MV irradiated at 312 nm for 30 minutes.

3. 5. 7. Pyrene

Pyrene has the ability to decrease the absorbance of MV by only %10. Figure 30 shows the UV-Vis spectra of pyrene (a) and PVC/pyrene/MV irradiated at 312 nm for 60 minutes (b). Again it is not as effective as HQ.

Table 4 gives the calculated percentage change in the absorbance of MV in the blends of PVC/MV with different sensitizers after irradiation at 312 nm for 30 minutes.

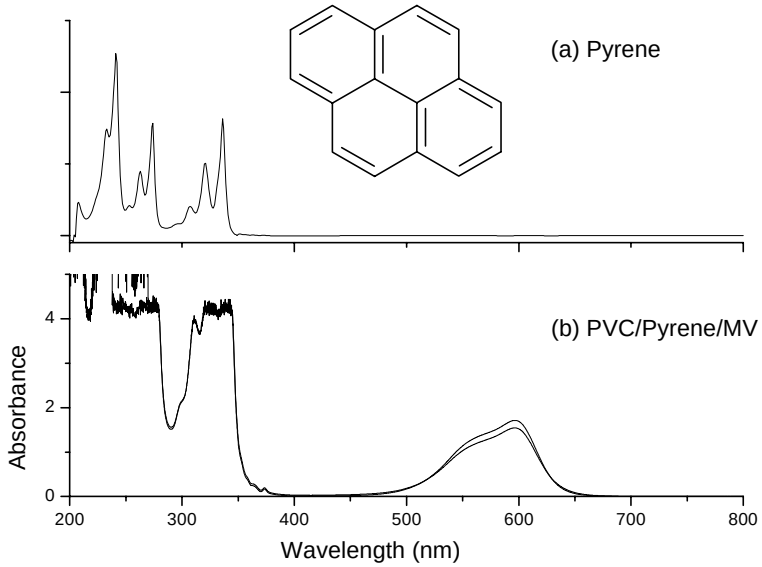


Figure 30: UV-Vis spectra of pyrene (a) and PVC/pyrene/MV irradiated at 312 nm for 30 minutes.

Table 4: Percentage change in the absorbance of MV at 590-nm exposed to 312 nm UV-light for 30 minutes.

Compounds	% Change in Absorbance of MV
Hydroquinone	42,2
Benzoquinone (+HQ)	16,8
Benzophenone	15,8
Pyrene	9,8
2-Acetonaphtanone	8,6
1,3,5-Trihydroxybenzene	4,5
4-Hydroxybenzoic Acid	2,6
Phenol	0
1-Naphtol	0

3. 6. Quenching

Since it is well established that HQ sensitizes the photodehydrochlorination of process, it should be possible to reverse the process by quenching the sensitization. For that purpose in this part of the thesis 1-nitronaphtalene and ascorbic Acid (which are well-established quenchers [63, 64]) are used as quenchers to understand the role of the excited triplet state of HQ in the mechanism of HQ assisted photodegradation of PVC at 312 nm UV light.

3. 6. 1. 1-Nitronaphtalene

Figure 31 shows the UV-Vis spectra of the indicated composition irradiated at 312 nm for 30 minutes. As shown in Figure 31a 1-nitronaphtalene does not show any sensitizer properties at this wavelength. It is obvious from Figure 31b that there is no

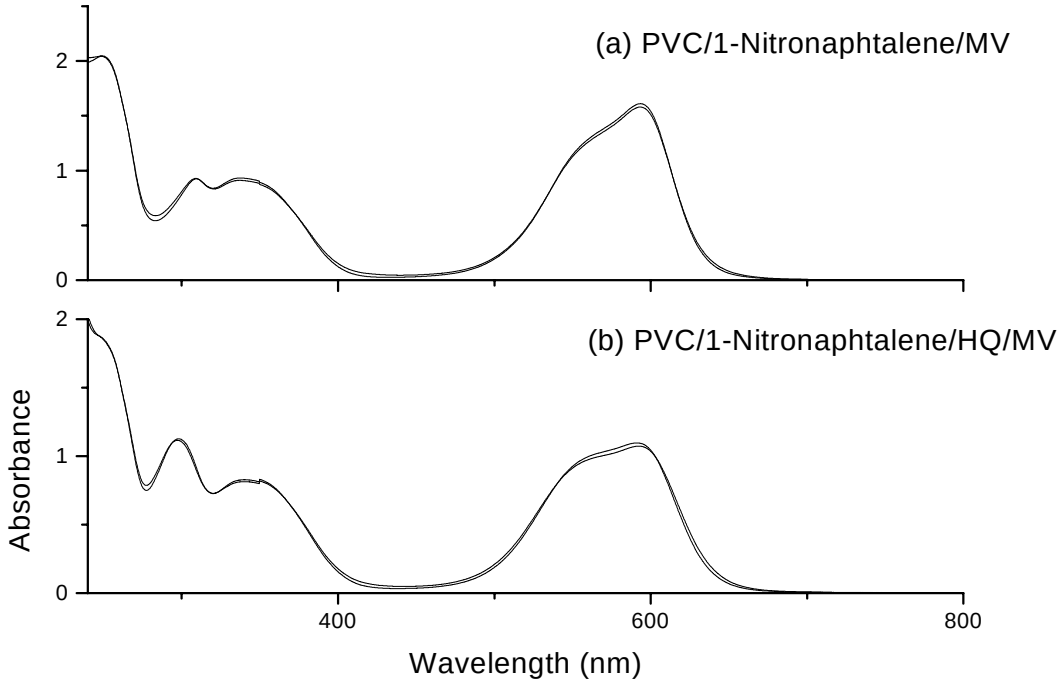


Figure 31: UV-Vis spectra of PVC/1-nitronaphtalene/MV (a) and PVC/1-nitronaphtalene/HQ/MV (b) irradiated at 312 nm for 30 minutes.

photodegradation in the presence of nitronaphtalene.

3. 6. 2. Ascorbic Acid

Figure 32 demonstrates the UV-Vis spectra of PVC/ascorbic acid/MV and PVC/ascorbic acid/HQ/MV irradiated at 312 nm for 30 minutes. As it can be inferred from the Figure 32a and 32b ascorbic acid does not exhibit any quenching because there is still a decrease in the absorbance of MV at 590-nm.

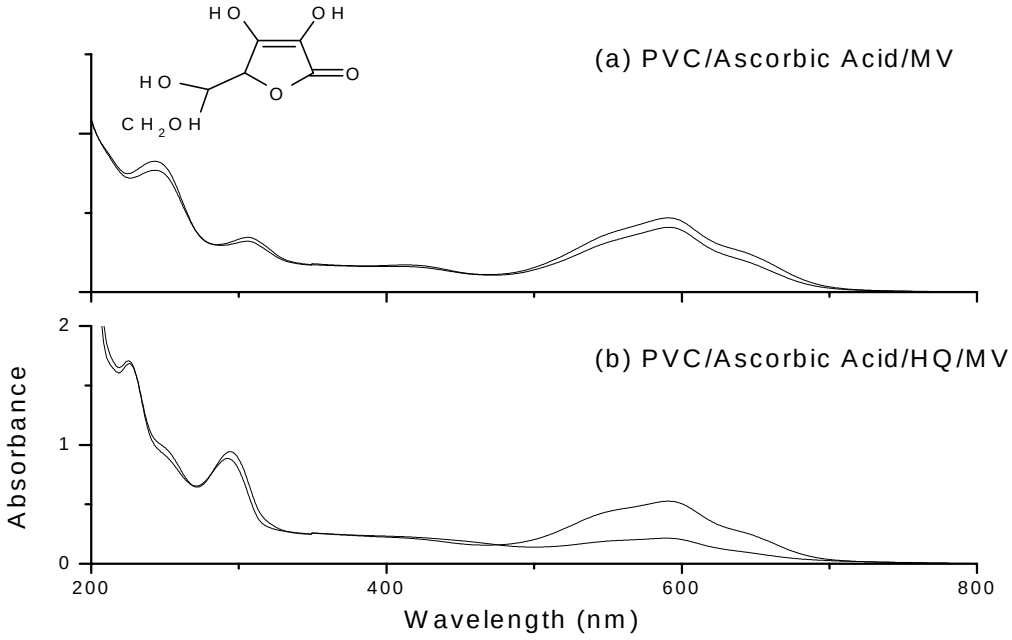


Figure 32: UV-Vis spectra of PVC/ascorbic acid/MV (a) and PVC/ascorbic acid/HQ/MV (b) irradiated at 312 nm for 30 minutes.

4. DISCUSSIONS

As has been mentioned in previous chapters, the main aim of this thesis is to determine the mechanism of HQ assisted photodegradation. In this section this is discussed in detail.

Although pure PVC dehydrochlorinates at 254 nm, it does not dehydrochlorinate at 312 nm. Addition of HQ to the PVC matrix facilitates the photodegradation of PVC at 312 nm UV light. Suzer et al. [17-19] studied photodehydrochlorination of PVC at different wavelengths and claimed that HQ sensitizes this process at 312 nm UV irradiation [20].

The potential of a polymer for light-induced degradation is determined by its ability to absorb photons of suitable energy and the availability of photochemical pathways to utilize the absorbed energy for chemical reactions. Only the radiation absorbed by a system is effective in producing chemical changes. Most polymers can absorb ultraviolet radiation of λ <300-nm, while those with chromophores such as carbonyl groups and unsaturated centers can absorb even longer wavelengths of ultraviolet radiation. The photon energies associated with the ultraviolet and visible radiation are in the same range as the bond dissociation energies of common covalent bonds in organic molecules including polymers. The unsubstituted C-C main chain bond and the C-H bond abundantly found in common polymers have bond energies in the range of 251-377 kJ/mol (480-320-nm), and 334-418 kJ/mol (350-250-nm), respectively. However, the C-Cl bond is somewhat weaker, 226 kJ/mol (530 nm), and can be broken more easily.

Hydroquinone has the properties of a good sensitizer (having φ_T=0.39, τ_T=1.3μs, and E_T= 311kJ mol^{-1}) [55, 59]. The major photoproduct resulting from the HQ-sensitized reaction is HCl produced from the PVC. This photoproduct was analyzed by putting acid trapping sides (methyl violet and PANI) in the matrix of the PVC and then observing the change in the process by using UV-Visible Spectroscopy [20]. One should remember the fact that this HQ assisted photodegradation involves ingredients; (i) 312 nm photons to provide the energy, (ii) HQ, to efficiently absorb this energy, (iii) PVC, to provide HCl, and (iv)

MV, to follow the process. Additional ingredients like BQ, sensitizers and quenchers may also play important roles.

i) Concentration of the HQ in the matrix of the PVC is a factor that affects the rate of PVC photodegradation. Critical HQ concentration for the onset of photodegradation is found to be 0.25 %. In order to effectively degrade PVC with HQ at 312 nm, one needs at least 0.25 % HQ in the blend. Once the critical concentration is reached, the rate of photodegradation becomes linearly increasing with HQ concentration. Since the proximity of all the three ingredients (HQ, PVC and MV) is needed for the process a critical concentration is thus not unexpected.

ii) Flux of the irradiation: Changing the number of photons coming to the surface of the blend changes the rate of the photodegradation. The primary consequences of the absorption of photon by the indicated compound are the occurrence of photophysical processes. Numbers of photons coming to the surface of the sample have direct relation with the number of photophysical processes [8, 10]. Then it is clear that the quantity of the incoming light is an important parameter in the rate of PVC photodehydrochlorination. In some photochemical processes, especially those involving rigid media, a certain threshold or incubation period is needed before a significant rate is achieved. This was the case in photoyellowing of PVC where the role of the primary photons was to create chromophores or polyenes (secondary or by-products), which can absorb photons more efficiently [57, 58]. Our experimental findings suggest only a linear dependence on the photon flux at 312 nm, as opposed to a certain threshold or other kinds of non-linear effects. Hence, the number of photons falling on the sample is one of the main factors in the rate-determining step of the HQ assisted photodehydrochlorination at 312 nm.

iii) Temperature of the medium is another key factor that affects the rate of photodegradation. Thermal dehydrochlorination of pure PVC has a temperature onset of 180^0C. Hence, one does not expect a temperature increase or decrease of 20K to significantly affect the rate of the photodegradation near the room temperature. However, it can increase the rate of HCl diffusion between the polymer chains to cause an effectively higher dehydrochlorination [8]. As was reported in the results section the UV induced dehydrochlorination in 30 minutes was determined as 48.6 % at 0 ^{0}C but 64.1 % at 20 ^{0}C. When these data are inserted in the Arrhenious equation activation energy of only ca. 10 kJ/mol is obtained. Such low activation energy only suggests that the effect of temperature can only be attributed to the diffusion of HCl rather than any chemical process.

iv) Intrinsic viscosity of the PVC is another factor that affects the rate of photodegradation. In this case different intrinsic viscosity corresponds to the different molecular weight and also structure. Xu et al. [62] discussed the effect of molecular weight on the PVC photodegradation. Figure 33a shows a clear formation of polyenes in low viscosity PVC in comparison with high viscosity PVC. The reason of higher amount of polyene formation (hence more dehydrochlorination) in low viscosity PVC may be attributed to the presence of higher amount of end groups in low viscosity, compared to the high viscosity PVC

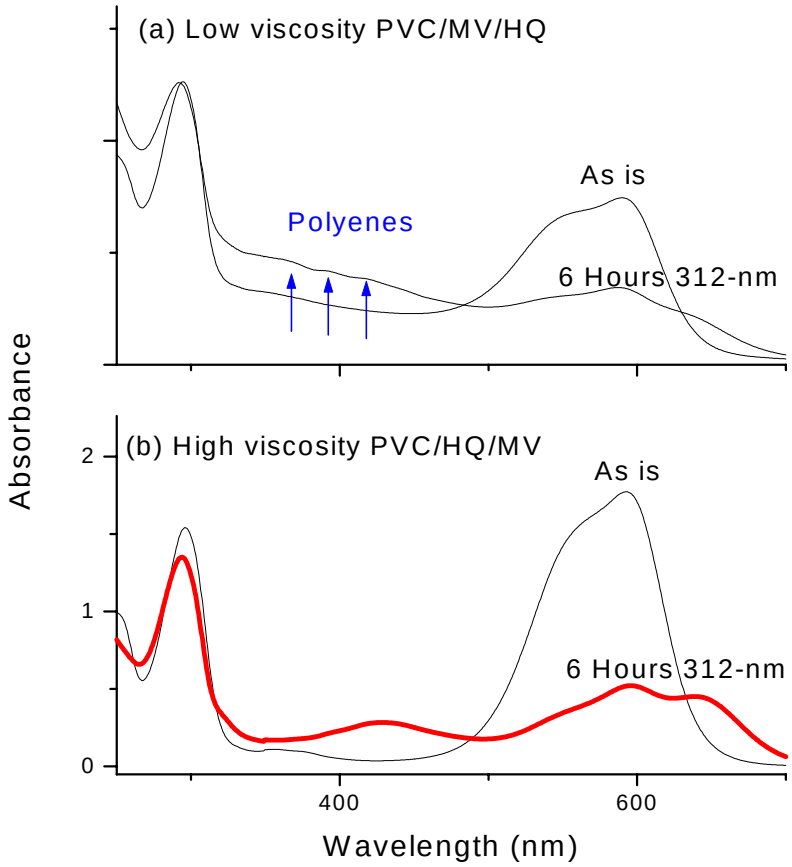


Figure 33: UV-Vis spectra of low viscosity PVC/HQ/MV (a) and high viscosity PVC/HQ/MV (b), irradiated at 312 nm for 6 hours.

v) Another factor that might affect the rate of PVC dehydrochlorination at 312 nm with HQ is the changing the hydroquinone-benzoquinone composition in the matrix of the sample. Since, the HQ/BQ is a redox couple, the presence of both have been claimed to be necessary for a process involving an oxidation-reduction process [55]. As was mentioned in the results section the benzoquinone does not have any effect on the rate of PVC dehydrochlorination. This fact largely eliminates the possibility that an oxidation-reduction type of a process is involved in the rate-determining step.

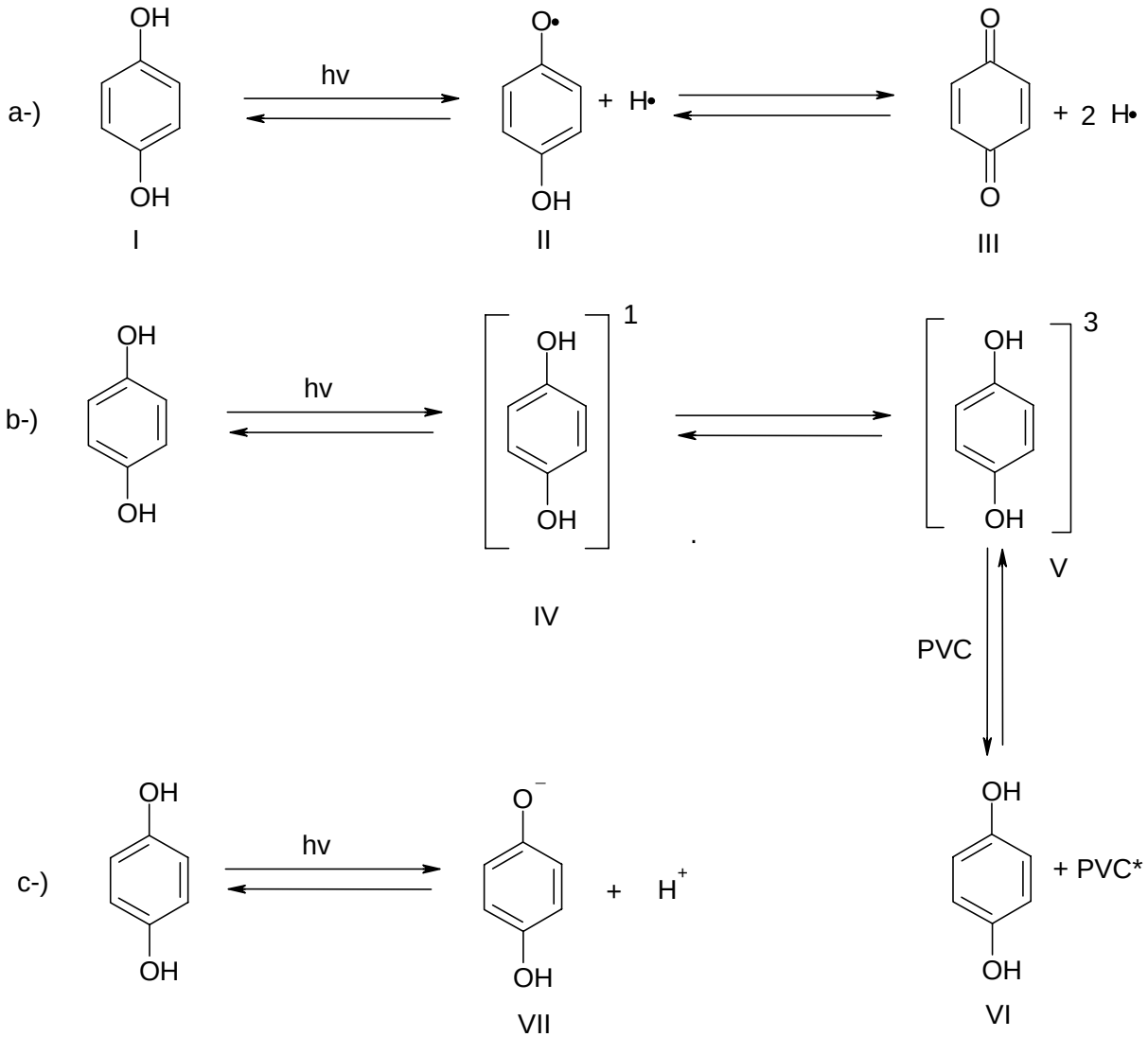
v) Sensitizers: Phenol, 1-naphtol, 1,3,5-trihydroxybenzene and 4-hydroxybenzoic acid are studied and they do not photodegrade PVC at 312 nm UV irradiation. By containing OH group and having aromaticity, they are similar in chemical structure to HQ however, their photochemical behavior at 312 nm are very different. Phenol, 1-naphtol and 1, 3, 5-

trihydroxybenzoic acid do not have absorbance at 312 nm and because of this they cannot sensitize the photodehydrochlorination of PVC at 312 nm. 1-Naphtol, has an absorbance band at 312 nm, but cannot photodegrade PVC at 312 nm either. Having absorbance at 312 nm is not the only prerequisite for photodehydrochlorination of PVC. In addition, the sensitizers should be able to transfer this absorbed energy to the PVC matrix efficiently. On the other hand, benzophenone, 2-acetonaptanone, pyrene and HQ have absorbance at 312 nm and they can photodegrade PVC at 312 nm. The mechanism of the benzophenone-assisted photodegradation of PVC is fully studied [10] and it involves formation of triplet state of benzophenone during irradiation of the benzophenone/PVC matrix. Absorption of a photon at 312 nm populates n➔π* singlet state (^{1}B) which undergoes intersystem crossing to form triplet benzophenone (^{3}B). Energy in the triplet state of benzophenone is believed to transfer to PVC by deexitation. A similar mechanism of triplet state formation in 2-acetonaptanone, pyrene and HQ is assumed to be involved.

vi) Quenchers are used to understand the effect of excited triplet state in the mechanism of PVC photodegradation by HQ. The unimolecular lifetimes of the triplet states are usually long enough so that diffusion of excited states and quenchers toward each other can compete favourably with intersystem crossing and phosphorescence [6, 7]. In this study, two quenchers ascorbic acid and 1-nitronaphtalene are used. Ascorbic acid is a well-known anti-oxidant (blocking the oxidation path) and 1-nitronaphtalene is an effective triplet quencher [63-65]. Ascorbic acid does not show any quenching. However, 1-nitronaptalene successfully blocks the photodegradation of PVC with HQ at 312 nm. In this case 1-nitronaptalene quenches the triplet state of HQ. This quenching of HQ /PVC film by nitronaphtalene can be explained by an electron transfer mechanism [10], in which electrons in the excited state are transferred from triplet state of the electron donor, HQ, to the electron acceptor,

nitronaphtalene. It is clear from the 1-nitronaphtalene experiment that HQ assisted photodegradation of PVC at 312 nm must involve a triplet state of HQ.

Scheme 10 shows three possible processes of HQ in the PVC matrix after absorption of 312 nm UV light. Scheme 10a shows the homolytic cleavage of O-H bond and scheme 10c shows the hetorolytic cleavage, whereas scheme 10b indicates the excitation of HQ from the ground state to the excited singlet state and then to the triplet state. In the light of sensitization findings it is possible to eliminate hetorolytic cleavage since 4-hydroxybenzoic acid is more acidic then HQ but there is no photodehydrochlorination of PVC/4-hydroxybenzoic acid at 312 nm irradiation. In addition in 4-hydroxybenzoic acids, carboxyl group is the electron-withdrawing group so that it should increase the poloration of O-H bond, which would facilitate the hetorolytic cleavage [2]. However, the rate of photodegradation with 4-hydroxybenzoic acids is very little as compared to the HQ. By the results of quenchers (1-nitronaphtalene) it can be stated that photodegradation follows the route of scheme 10b. In other words, in order to photodegrade PVC at 312 nm UV light with the help of HQ, reaction should cross to the triplet state. For very long times irradiation, scheme 10a may also be operative since 12 hours irradiation of the films of PVC/HQ shows a strong decrease in the O-H stretching of the HQ in the IR spectrum. However, during irradiation of the PVC/HQ at 312 nm UV light for 60 or 120 minutes there is not any significant change in the absorbance of HQ in the UV-Vis spectrum.



Scheme 10: Possible processes of HQ in the PVC matrix after 312 nm UV light absorption.

To sum up, HQ assisted photodegradation of PVC at 312 nm follows the triplet state formation of HQ. Flux of the irradiation, concentration of the HQ, temperature of the medium, intrinsic viscosity of the PVC, and hydroquinone-benzoquinone composition of the sensitizer are the parameters that have been taken into consideration for understanding the HQ assisted PVC photodehydrochlorination at 312 nm UV light. Sensitizers and quenchers are crucial in terms of understanding the type of mechanism that is dominant in the photodehydrochlorination of PVC/HQ at 312 nm.

5. CONCLUSIONS

In this thesis, mechanism of HQ assisted PVC photodehydrochlorination at 312 nm is discussed in detail. The effect of concentration of HQ in the matrix of PVC, benzoquinone-hydroquinone ratio in the PVC matrix, the temperature of the medium, the viscosity of the PVC, the flux of the irradiation on the rate of photodehydrochlorination at 312 nm have been investigated. Quenching of PVC/HQ with nitronaphtalene gives an important clue about the triplet state formation of HQ. It is proposed that HQ assisted photodehydrochlorination of PVC at 312 nm involves triplet state formation of HQ and transfer of this triplet state energy to the PVC.

Further experiments should be carried out in order to find other model compounds like HQ, and benzophenone in order to increase the wavelength of the irradiation. The theoretical value of activation energy for dehydrochlorination of a C-Cl bond is 226kJ/mol, which corresponds to 530-nm. Using suitable sensitizers it may be possible to increase the wavelength of the irradiation from 312 nm to the higher wavelengths into the visible region. By increasing the wavelength of the irradiation one can decrease the damage of the irradiation on the PVC backbone. Hopefully, using longer irradiation wavelengths may produce longer polyene chains.

6. REFERENCES

[1] K. Mulder, and M. Knot, “PVC Plastic”, *Tech. in Soci.*, vol. 23, pp. 265-286, 2001

[2] R.T. Morrison, R. N. Boyd, *Organic Chemistry*, Allyn and Bacon, Inc., New York, 1987.

[3] F. W. Billmeyer, LR, *Textbook of Polymer Science*, Wiley-Interscience, Inc., New York, 1971.

[4] R. J. Young and P. A. Lovell, *Introduction to Polymers*, Chapman&Hall, New York, 1991.

[5] A. Dimian, D. V. Diepen, G. A. van der Wall, “Dynamic Simulation of a PVC Suspension Reactor”, *Computers Chem.Engng*.,vol. 19, pp. S427-S432, 1995.

[6] J. F. Rabek, *Mechanism of Photophysical Processes and Photochemical Reactions in Polymers*, John Wiley & Sons, New York, 1987.

[7] E. Reichmanis, J. H. O. Donnel, *The Effects of Radiation on High-Technology Polymers*, American Chemical Society, New York, 1989.

[8] W. Schnabel, *Polymer Degradation*, Hanser International, New York, 1981.

[9] A. L. Andrady, "Photodegradation", *Adv.Polym. Sci*., vol. 128, pp. 48-77, 1997.

[10] E. D. Owen, R.J. Balley, "Photosensitized Dehydrochlorination of PVC", *J.Polym. Sci.*, vol. 10, pp. 113-122, 1972.

[11] D. E. Winkler, "Mechanism of PVC Degradation and Stabilization", *J. Polym. Sci.,* vol. 35, pp. 3-16, 1959.

[12] L. Jian, Z. Dafei, Z. Deren, "The Photodegradation of PVC", *Polym. Deg. Stability*, vol. 31, pp. 1-7, 1991.

[13] B. E. Kohler, J. C. Woehl, "A Simple Model for Conjugation Lengths in Polyene Chains", *J.Chem.Phys*., vol. 103, pp. 6253-6256, 1995.

[14] J. L. Gardette, S. Gaument, J. L. Philippart, "Influence of the Experimental Conditions on the Photooxidation of PVC", *J. App. Polm. Scie.*, vol. 48, pp. 1885-1895, 1993.

[15] R. Bacaloglu, M. Fisch, "Degradation and Stabilization of PVC", *Polym. Deg Stability*, vol. 47, pp. 9-32, 1995.

[16] C. Decker In: J. L. Benham, J. F. Kinstle (eds) *Chemical Reactions on Polymers*, ACS, New York, 1988.

[17] Ö. Birer and S. Süzer, "UV-induced Acid–base Chemistry Within the PVC Matrix", *Polymer*, vol. 42, pp. 1833-1835, 2001.

[18] U. A. Sevil, O. Güven, Ö. Birer and S. Süzer, " Doping of 2-Cl-PANI/PVC Films by Exposure to UV, Rays and e-beams", *Synth Metals*, vol. 110, pp. 175-179, 2000.

[19] O. Birer, S. Suzer, U. A. Sevil and O. Guven, " UV–Vis, IR and XPS Analysis of UV Induced Changes in PVC Composites", *J. Mol. Struct*., vol. 482-483, pp. 515-518, 1999.

[20] S. Suzer, O. Birer, A. U. Sevil and O. Guven, "UV-Induced Electrical and Optical Changes in PVC Blends", *Chemical Monthly*, vol. 132, pp. 185-192, 2001.

[21] J. Roncali, "Synthetic Principles for Bandgap Control in Linear π-Conjugated Systems", *Chem. Rev.*, vol. 97, pp. 173-205, 1997.

[22] A. G. Macdiarmid, "Synthetic Metals: A Novel Role for Organic Polymers", *Synth. Metals*, vol. 125, pp. 11-22, 2002

[23] J. Tang, X. Jing, B. Wang and F. Wang, "Infrared Spectra of Soluble PANI", *Synth. Metals*, vol. 24, pp. 231-238, 1988.

[24] N. S. Sariciftci, L. Smilowitz, Y. Cao and A. J. Heeger, "Absorption Spectroscopy of Nonlinear Excitation in PANI", *J.Chem.Phys*., vol. 98, pp. 2664-2669, 1993.

[25] A. P. Monkman, D. Bloor, G. C. Stevens and J. C. H. Stevens, "Electronic Energy Levels of PANI", *J.Phys.D: Appl. Phys.,* vol. 20, pp. 1337-1347, 1987.

[26] N. Stertova, B. Geffroy, J. M. Nunzi, I. Petkov, "PVC as a Photodonor of HCI for Protonation of PANI", *J. Photochem. Photobio. A: Chem.,* vol. 113, pp. 99-101, 1998.

[27] T. Makela, S. Penman, S. Jussila, H. Isotalo, "Lithographic Patterning of Conducting PANI", *Synth. Metals*, vol. 101, pp. 705-706, 1999.

[28] M. Wan, M. Li, J. Li, and Z. Liu, "Transparent and Conducting Coatings of PANI Composites", *Thin Solid Films*, vol. 259, pp. 188-193, 1995.

[29] D. C. Harris, *Quantitative Chemical Analysis*, 3rd edition, W.H.Freeman and Company, New York, 1991.

[30] S. Denman, S. Jameel, J. Hay, J. K. Suyden, "Photostability of Crystal Violet", *Dyes Pigments*, vol. 30, pp. 67-72, 1996.

[31] Y. B. Shim, S. M. Park, "Spectroelectrochemical Studies of p-Benzoquinone Reduction in Aqueous Media", *J. Electroanal. Chem*., vol. 425, pp. 201-207, 1997.

[32] D. C. Harris, M. D. Bertolucci, *Symmetry and Spectroscopy*, Dover Publication, Inc., New York, 1978.

[33] D. A. Skoog, *Principles of Instrumental Analysis*, Harcourt Brace College Publishers, New York, 1992.

[34] J. D. Ingle, S. R. Crouch, *Spectrochemical Analysis*, Prentice Hall, New York, 1988.

[35] M. J. K. Thomas, *Ultraviolet and Visible Spectroscopy*, John Wiley & Sons, New York, 1996.

[36] B. Stuart, *Modern Infrared Spectroscopy*, John Wiley & Sons, New York, 1996.

[37] D. Briggs and M. P. Seah, *Practical Surface Analysis*, vol.1, John Wiley & Sons, New York, 1983.

[38] D. Braun and D. Hepp, "Investigation on the Stabilization of PVC by Metal Soaps", *J. Polym. Sci.,* vol. 33, pp. 307-313, 1971.

[39] Dr. D. Stevenson, M. Harr, B. Hood and T. Jennings, " Flexible PVC Stabilization: the Phosphite Approach"*, Plast. Additi. Compo*., Vol. 4, pp. 28-32, 2002

[40] E. Tsuchida, C. Shin, I. Shinohora and S. Kambara, "Synthesis of a Polymer Chain Having Conjugated Unsaturated Bonds by Dehydrochlorination of Polyhalogen-Containing Polymers ", *J.of Polym. Sci.: Part A*, vol. 2, pp. 3347-3354, 1964.

[41] K. Soga, M. Nakamanu, Y. Kabayashi and S. Ikeda, "Electrical and Physical Properties of a Polyene Arising From Dehydrochlorination of PVC", *Synth. Metals*, vol. 6, pp. 275-283, 1983.

[42] T. Danno, H. Kondoh, K. Furuhata and K. Miyasaka, “Synthesis, Structure, and Properties of Conjugated Polyene Films by Dehydrochlorination of PVC films”, *J.of Appl. Polym. Sci.,* vol. 29, pp. 3171-3184, 1984.

[43] C. Decker, "Synthesis of Conductive Polymers by Laser Irradiation of Chlorinated PVC", *J. Polym. Sci.,* vol. 25, pp. 5-10, 1987.

[44] P. Simon, F. Cernay and L. Valko, “On the Possibility of Both-Sided Polyene Sequences Growth in the Dehydrochlorination of PVC", *Eur. Polym. J*., vol. 25, pp. 531-533, 1989.

[45] Z. Hell, Z. Junakovic, F. Ranogajec, I. Duornik, M. Baric, “Application Problems of PVC Materials Irradiated with High Doses”, *Makromol.Chem., Makromol. Symp*., vol. 29, pp. 267-275, 1989.

[46] A. Perichaurd, P. Bernier, M. Audenaert, S. Lefrant, “Dehydrochlorinated PVC”, *Solid State Comm.*, vol. 72, pp. 413-418, 1989.

[47] L. N. Sidney, D. C. Lynch and P. S. Willet, “A New Radiachromic Dosimeter Film”, *Radiat. Phys. and Chem.,* vol. 35, pp. 779-782, 1990.

[48] K. Ogura, J. Yana, K. Kisaka and H. Goto, “Novel Preperation of Electrically Conducting PVC by Photo-dehydrochlorination from PVC/PPy Composite Film”, *J. Polym. Sci.: Part A: Polym. Chem*., vol. 32, pp. 33-38, 1994.

[49] B. E. Kohler, I. D. W. Samuel, “Experimental Determination of Conjugated Lengths in Long Polyene Chains”, *Chem.Phys.*, vol. 103, pp. 6248-6252, 1995.

[50] R. Benavides, M. Edge, N. S. Allen, M. M. Tellez, “Polyene Formation in PVC Stabilised with Pre-heated Metal Stearates”, *Polym. Bulletin,* vol. 42, pp. 273-279, 1999.

[51] N. Sertova, B. Geffrag, J. M. Nunzi, I. Petkov, "PVC As Photodonor of HCl for Protonation of Polyaniline", J. *of Photochem. and Photobio. A: Chem*., vol. 113, pp. 99-101, 1998.

[52] V. P. Parkhutic and E. Matveeva, "Effects of Molecular Doping by Hydroquinones on Morphology and Optical Properties of PANI", *J. Phys. Chem.* B, vol. 102, pp. 1549-1555, 1998.

[53] A. Torikai, H. Hasegawa, "Accelerated Photodegradation of PVC", *Polym. Deg. Stability*, vol. 63, pp. 441-445, 1999.

[54] L. Guo, G. Shi, Y. Liang, "Polyene Films Prepared by PEG-Catalysed Dehydrochlorination of PVC", *Synth. Metals*, vol. 104, pp. 129-135, 1999.

[55] U. P. Agarwal, "On the Importance of Hydroquinone/Quinone Redox System in the Photoyellowing of Mechanical Pulps", *10th International Symposium on Wood and Pulping Chemistry*, TAPPI Press, vol. 1, pp. 694-697, 2000.

[56] L. Duic and S. Grigic, "The Effect of PANI Morphology on Hydroquinone / Quinone Redox Reaction", *Electrochimica Acta*, vol. 46, pp. 2797-2803, 2001.

[57] R. J. Foster, P. H. Whitling, J. M. Mellor and D. Phillips, "Photosensitized Dehydrochlorination of PVC-I", *J. of Appl. Polym. Sci*., vol. 22, pp. 1129-1134, 1978.

[58] S. Hirayama, R. J. Foster, J. M. Mellur, P. H. Whitling, K. R. Grant and D. Phillips, "The Sensitized Photodehydrochlorination of PVC-II", *Eur. Polym. J.,* vol. 14, pp. 679-684, 1978.

[59] C. Richard, D. Vialaton, J.P. Auger, F. Andreux, "Transformation of Monuron Photosensitized by Soil Extracted Humic Substances", *J. Photochem. Photobio. A: Chem.*, vol. 111, pp. 265-271, 1997.

[60] M. Celina, D. K. Ottesen, K. T. Gillen and R. L. Clough, "FTIR Emission Spectroscopy Applied to Polymer Degradation", *Polym. Degradation and Stability*, vol.58, pp.15-31, 1997.

[61] J. Tang, X. Jing, B. Wang and F. Wang, "Infrared Spectra of Soluble PANI", *Synthetic Metals*, vol. 24, pp. 231-238, 1988.

[62] P. Xu, D. Zhou and D. Zhau, "Studies of the Thermal Stability of PVC", *Eur. Polm. J.*, vol. 25, pp. 581-583, 1989.

[63] D. Patra, A. K. Mishra, "Fluorescence Quenching of Benzo [k] fluoranthene in Poly(vinyl alcohol) Film", *Sens. Actuators B*, vol. 80, pp. 278-282, 2001.

[64] D. Angelescu and M. Vasilescu, "Quenching of Pyrene Derivatives Fluorescence by Nitroxide Radicals in Sodium Dodecyl Sulfate Micellar Solutions", *J. Colloid Interface Sci.*, vol. 244, pp. 139-144, 2001.

[65] B. Marcinak and G. L. Hug, "Quenching of triplet State of Organic Compounds by 1, 3-Diketonate Transition-Metal Chelates in Solution", Coord. Chem. Rev., vol. 159, pp. 55-74, 1997.